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PHYSICOCHEMICAL CHARACTERIZATION OF HIGH-PERFORMANCE FIBRE-REINFORCED ORGANIC-MATRIX COMPOSITES

PART 6. METHODS FOR QUALITY CONTROL OF MATRIX CHEMISTRY

by

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PREFACE

This report is the sixth and last of a series resulting from a cooperative effort involving the Industrial Materials Research Institute (IMRI) of the National Research Council Canada (NRCC) (Boucherville, Québec) and Canadair Limited (Montréal, Québec). The subject is one of growing importance in high-technology manufacturing, namely the physicochemical characterization of high-performance fibre-reinforced organic-matrix composites. The first report in the series gives a general discussion and literature review of the subject. The second, third, and fourth describe in detail the development of various analytical methods for a typical graphite-epoxy prepreg, Narmco Rigidite 5208/WC3000, while the fifth concerns the use of these methods to monitor the aging of that system. This final report summarizes the contents of the previous ones and also describes the application to some other commercial systems of the methods developed for Narmco 5208. The titles of the complete series are as follows:

Part 1. General Discussion and Literature Review
Part 2. Applications of Infrared Spectroscopy
Part 3. Applications of Liquid Chromatography
Part 4. Applications of Pyrolysis Gas Chromatography and Thermal Analysis
Part 5. A Study of the Room-Temperature Aging of Narmco 5208/WC3000 Prepreg
Part 6. Methods for Quality Control of Matrix Chemistry

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SUMMARY

Over the past ten to fifteen years, considerable interest has developed in the use of physicochemical analysis methods for quality control of thermoset resins used in high-performance composite materials. This report is a summary of recent research performed at NRCC's Industrial Materials Research Institute with the aim of developing faster and more reliable methods for such applications.

In the first stage of the work, optimized methods were developed for a typical commercial carbon-epoxy system, Narmco Rigidite 5208/WC3000. The techniques employed are Fourier transform infrared spectroscopy, liquid chromatography, thermal analysis, and pyrolysis — gas chromatography.

In Fourier transform infrared spectroscopy (FT-IR), three different methods of obtaining the spectrum were evaluated: transmission of a thin film of resin, attenuated total reflection of prepreg, and diffuse reflection of prepreg or cured composite. The transmission method requires solvent extraction of the resin from the prepreg and casting of a thin film on a transparent window. Although it is an accepted method for the quantitative analysis of such resins, it is shown to be subject to considerable error due to nonuniform thickness of cast films. Very careful sample preparation is needed to give acceptable results. The attenuated total reflection method was found to be better for quantitative analysis because it gives more reproducible results and can be applied directly to prepreg. This avoids the problem of nonuniform thickness and also results in considerable time savings in sample preparation. The diffuse reflection method is not recommended for quantitative work with composites because it is subject to variations due to front-surface (Fresnel) reflection and scattering effects. However, it is a good method for qualitative work because it allows measurement of both uncured and cured samples with practically no sample preparation. It can be used, for instance, as a nondestructive method for confirming completion of cure in finished parts.

Liquid chromatography is generally more time-consuming than infrared spectroscopy but provides more detailed information and is more sensitive to small variations in chemical composition. Improved methods were developed using three techniques: reverse-phase liquid chromatography (RPLC), high-speed reverse-phase liquid chromatography (HS-RPLC), and high-performance size-exclusion chromatography (HPSEC). The RPLC method uses gradient elution with acetonitrile/water as eluent and acetophenone as internal standard. Excellent separation is achieved in 25 minutes, with a total analysis time of about one hour, allowing for regeneration of the column. With high-speed RPLC, using short columns packed with 3 µm particles, it has been shown that samples can be analyzed in only 10 minutes, including column regeneration. Although the resolution is not quite as good as with conventional columns, the method is probably acceptable for routine control purposes and would result in significant savings in time and materials. The HPSEC method developed is also an improvement over published methods. Using a single column packed with 5 µm particles of highly crosslinked styrene-divinylbenzene copolymer, good chromatograms are obtained in less than 8 minutes. SEC is particularly useful for obtaining information on the degree of polymerization of the resin.

In thermal analysis, differential scanning calorimetry (DSC) is used to study the kinetics of cure of the resin and to measure the heat of polymerization ΔH. In the case of prepreg, because the sample used for analysis is relatively small the percentage of resin may vary significantly from specimen to specimen. To obtain an accurate value for ΔH, the percentage should be determined for each specimen. A thermogravimetric analysis (TGA) method has been developed for this purpose. It has been shown that, using an oxygen atmosphere, the decomposition of the resin and the oxidation of the carbon fibres are sufficiently distinct to allow accurate determination of the percentage of resin.

The pyrolysis - gas chromatography technique has also been studied. Its major advantage, compared to the techniques just described, is that it can be applied to the composite at all stages of cure. The pyrolysis - gas chromatogram is a detailed "fingerprint" of the resin and also can be used as a quantitative tool in certain cases, such as for determining the ratio of epoxy resin to amine hardener.

The second stage of the project involved a comprehensive study of the changes occurring in Narmco 5208/WC3000 prepreg when it is exposed to ambient temperature and 50% R.H. for periods up to 66 days. It was shown that the system undergoes significant changes in chemistry, mainly gradual polymerization, and that these are easily and accurately detected using the methods developed in the first stage. Certain physical properties, notably the gel time, are also affected. Such changes would almost certainly affect the processing and properties of complex parts made from the prepreg. However, when simple test panels were made in the laboratory and subjected to mechanical testing, any effects of the prepreg aging were masked by the scatter associated with the mechanical testing. These results do not indicate that the aging is insignificant, but rather that standard laboratory mechanical tests are not sufficiently sensitive to detect important chemical changes which could have detrimental effects on complex parts made in the factory environment. This underlines the importance of using sensitive physicochemical test methods for proper process control.

In the third stage of the project, some of the methods developed for Narmco 5208/WC3000 were applied without modification to a number of other commercial systems, generally with good results. In all cases, the liquid chromatography methods gave detailed chromatograms which would be suitable for quality control if some further work were done to identify the most important peaks. The infrared spectroscopic methods are also generally applicable, with certain exceptions. For instance, the attenuated total reflection method is of limited value for systems containing the hardener dicyandiamide (DICY), because of the insolubility of DICY in most epoxy resins at room temperature. Also, diffuse reflection provides less information in the case of systems reinforced with Kevlar or glass fibres than it does in carbon-fibre systems, because there is less reflection at the matrix-fibre interface.

RÉSUMÉ

Depuis les 10 ou 15 dernières années, l'utilisation des méthodes physicochimiques pour le contrôle de qualité des résines thermodurcissables employées dans les matériaux composites à haute performance s'est considérablement accrue. Ce rapport est un résumé des travaux récents réalisés à l'Institut de génie des matériaux du CNRC dans le but de développer des méthodes de caractérisation plus rapides et plus précises.

Dans la première étape de ce travail, des méthodes améliorées ont été développées à l'aide d'un système commercial à base de fibre de carbone et résine époxyde (Narmco Rigidite 5208/WC3000). Les techniques utilisées sont la spectroscopie infrarouge à transformée de Fourier, la chromatographie liquide, l'analyse thermique, et la chromatographie en phase gazeuse couplée à la pyrolyse.

En spectroscopie infrarouge à transformée de Fourier (SIRTF), trois méthodes différentes ont été étudiées pour obtenir un spectre infrarouge, soit la transmission avec un mince film de résine, la réflexion interne du préimprégné, et la réflexion diffuse du préimprégné ou du composite durci. La méthode de transmission nécessite l'extraction de la résine du préimprégné à l'aide d'un solvant organique, suivi de la déposition d'un mince film sur une fenêtre transparente. Bien que cette méthode soit généralement acceptée pour l'analyse quantitative de telles résines, il est montré qu'elle est sujette à des erreurs considérables résultant de la non-uniformité de l'épaisseur des films. Une préparation soignée de l'échantillon est nécessaire pour obtenir des résultats acceptables. La méthode de réflexion interne est préférable pour l'analyse quantitative car elle peut être appliquée directement au préimprégné et la reproductibilité est aussi fortement améliorée. De plus, le temps d'analyse est substantiellement réduit et le problème de non-uniformité de l'épaisseur du film est éliminé. La méthode de réflexion diffuse n'est pas recommandée pour une analyse quantitative des composites car il y a des variations causées par la réflexion de surface (Fresnel) et la diffusion. Cependant, il s'agit d'une bonne méthode pour l'analyse qualitative car elle permet d'obtenir des spectres sans aucune préparation sur des échantillons non-durcis et durcis. Elle peut être utilisée comme méthode non-destructive pour confirmer la fin du durcissement dans les pièces finies.

La chromatographie liquide, bien que nécessitant un temps d'analyse plus long, génère plus d'informations, et est plus sensible aux faibles variations dans la composition chimique. Des méthodes améliorées ont été développées en utilisant trois techniques: la chromatographie liquide en phase inversée (CLPI), la chromatographie liquide en phase inversée à haute vitesse (CLPI-HV) et la chromatographie d'exclusion à haute performance (CEHP). La méthode CLPI utilise un gradient d'élution avec un éluant acétonitrile/eau et l'acétophénone comme standard interne. Une excellente séparation est réalisée en moins de 25 minutes avec un temps total d'analyse d'une heure en incluant la regénération de la colonne. En CLPI à haute vitese, l'analyse complète peut être réalisée en moins de 10 minutes à l'aide d'une courte colonne remplie avec des particules de 3 µm. Bien que la résolution ne soit pas aussi bonne que sur les colonnes conventionnelles, cette méthode est probablement acceptable pour un contrôle de qualité et résulte en des gains significatifs en temps et en matériaux. La méthode CEHP utilise une colonne remplie de particules de 5 µm d'un gel de poly(styrène-divinylbenzène) hautement réticulé. La séparation est obtenue

en moins de 8 minutes. Cette technique est particulièrement utile pour obtenir des informations sur le degré de polymérisation de la résine.

En analyse thermique, la calorimétrie différentielle à balayage est utilisée pour étudier la cinétique de durcissement de la résine et pour mesurer la chaleur de polymérisation DH. Pour le préimprégné, le pourcentage de résine varie significativement d'un échantillon à un autre car la taille de celui-ci est relativement petite. Le pourcentage de résine doit être déterminé dans chaque échantillon pour obtenir une valeur exacte de DH. Une méthode thermogravimétrique a été développée à cet effet. La décomposition de la résine et l'oxydation de la fibre de carbone en atmosphère d'oxygène sont suffisamment distinctes pour permettre une détermination exacte du pourcentage de résine.

La chromatographie en phase gazeuse couplée à la pyrolyse a aussi été étudiée. Son avantage majeur par rapport aux techniques précédentes est qu'elle peut être appliquée à toutes les étapes du durcissement. Le chromatogramme obtenu est un profil détaillé de la résine et il peut être utilisé dans certains cas pour déterminer le rapport époxyde - durcisseur amine.

La deuxième partie du projet consistait à étudier les variations dans le système Narmco 5208/WC3000 lors d'une exposition à la température ambiante et à 50% d'humidité relative pour une durée de 66 jours. Il a été montré que le système subit des changements chimiques importants, soit principalement une polymérisation graduelle de la résine, et que ceux-ci sont facilement détectés par les méthodes décrites précédemment. Certaines propriétés physiques comme le temps de gélation sont aussi affectées. Ces variations influencent certainement la mise-en-forme et les propriétés finales des pièces complexes fabriquées à partir du préimprégné. Cependant, lorsque des panneaux simples sont fabriqués au laboratoire et caractérisés par des tests mécaniques, les effets du vieillissement du préimprégné sont masqués par l'erreur associée aux tests mécaniques. Ces résultats n'indiquent pas que le vieillissement est non significatif mais plutôt que les tests mécaniques standards ne sont pas suffisamment sensibles pour détecter des changements chimiques importants qui pourraient avoir des répercussions sur les pièces complexes fabriquées en usine. Ceci souligne l'importance des méthodes physicochimiques pour un contrôle de qualité approprié.

Dans la troisième partie de ce travail, les méthodes développées pour le système Narmco 5208/WC3000 ont été appliquées sans modification, généralement avec de bons résultats, à un certain nombre de systèmes commerciaux. Dans tous les cas, la chromatographie liquide donne des chromatogrammes détaillés qui pourraient être adéquats pour le contrôle de qualité si un travail supplémentaire était réalisé pour identifier les pics principaux. La spectroscopie infrarouge est aussi généralement applicable avec certaines exceptions. La réflexion interne est d'utilisation limitée pour les systèmes contenant le durcisseur dicyandiamide (DICY) car il est insoluble dans la plupart des résines époxydes à la température de la pièce. De plus, la réflexion diffuse fournit moins d'information dans le cas des systèmes renforcés avec des fibres de Kevlar ou de verre par rapport aux fibres de carbone car il y a moins de réflexion à l'interface matrice-fibre.

1. INTRODUCTION

This report is the sixth and last of a series concerned with the application of physico-chemical testing methods to high-performance composite materials consisting of high-strength reinforcing fibres (glass, carbon, Kevlar®) embedded in an organic polymer matrix (epoxy, polyimide, polyester, etc.). As outlined in the first report [1], the objective of the research project, a collaboration between the Industrial Materials Research Institute of the National Research Council Canada and Canadair Inc. of Montréal, was to develop improved methods for the rapid and accurate characterization of the chemical composition of the organic matrix materials. Such methods are becoming more common in quality control laboratories as the applications of composite materials grow, particularly in the aerospace industry. The high cost, in both materials and labour, of the large parts being manufactured, together with their use in critical applications such as aircraft primary structures, has increased the need for highly stringent control methods to ensure the quality of the finished parts.

Unlike metal alloys or thermoplastics, the thermosetting resins currently used in most fibre-reinforced composites are based on mixtures of chemicals which undergo complex reactions during formulation, storage, and processing. Variations in chemical composition can have significant effects on the processing behaviour (especially the rheology) and the final properties (both short- and long-term) of such materials. Good manufacturing procedure therefore requires an appreciation of the chemistry involved and a knowledge of how to analyze and control it. In recent years, a considerable amount of effort has been devoted to this subject, mainly involving "high-performance" composites based on epoxy or polyimide resins and carbon or Kevlar® fibres. Composites based on polyester and fibreglass are usually used in less critical applications which do not justify the added cost of extensive chemical characterization.

The first report in this series [1] gives a general discussion of the subject and a comprehensive review of the recent literature including some 300 references. The second to fifth reports [2-5] describe in detail the recent efforts of this laboratory to develop expertise in the field and to improve the state of the art. Specific analytical methods have been developed using various techniques, namely infrared spectroscopy [2], liquid chromatography [3], thermal analysis and pyrolysis - capillary gas chromatography [4]. Practically all the work described was done using one particular carbon-epoxy composite system, Narmco Rigidite 5208/WC3000. In addition, the methods developed have been applied to a particular problem — the aging of the carbon-epoxy prepreg when it is exposed to ambient temperature and humidity [5]. Under these circumstances, the components of the mixture undergo premature reaction which affects the physical properties and processing behaviour of the system.

The object of this report is twofold. Firstly, it summarizes the most important results of the previous five and gives the optimized methods developed using Narmco 5208. Secondly, it describes some results obtained when these methods are applied to other commercial systems. The applicability of these methods is by no means limited to the aerospace industry. Other fields where they can be valuable include structural adhesives and the manufacture of printed circuit boards.

2. DEVELOPMENT OF METHODS FOR NARMCO 5208

2.1 THE NARMCO 5208 SYSTEM

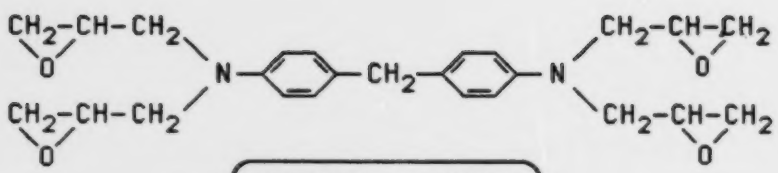
The composite system chosen for intensive study was Rigidite 5208/WC3000-42", sold by Narmco Materials, Inc. (Anaheim, California). The reinforcement consists of Celion carbon fibres, 3000 fibres per yarn, woven in an 8-harness satin pattern. The woven fabric is impregnated with Narmco 5208 resin to a nominal resin content of 42% by weight and the prepreg is supplied on a plastic backing sheet in rolls 42 inches wide. The recommended cure schedule consists of a one-hour dwell at 275°F (135°C) followed by a two-hour cure at 350°F (177°C).

It has been reported [6] that Narmco 5208 resin consists primarily of three components: two epoxy resins and an amine hardener. The major epoxy, which accounts for about 69% by weight, is based on TGDDM (tetraglycidyldiaminodiphenylmethane). A common commercial product of this type is Ciba-Geigy Araldite MY 720. The second most important component (about 22% by weight) is the curing agent DDS (diaminodiphenylsulphone); an example of a commercial grade of this material is Ciba-Geigy Hardener HT 976. The third component (about 9% by weight) is the minor epoxy, which is of the bisphenol A Novolac type (for example, Celanese Epi-Rez SU-8). It contains the monomer DGEBA (diglycidyl ether of bisphenol A). The chemical structures of these materials are given in Figure 1. The DDS is a relatively pure material, but the epoxy resins consist of a mixture of monomer, oligomers, and other products (starting materials and by-products). A more detailed discussion of the Narmco 5208 system, including composition, analysis, and the nature of the curing reaction, is given in an earlier report [1]. Several other commercial systems (for example, Hercules 3501 and Fiberite 934) are also based on TGDDM and DDS but contain different minor components.

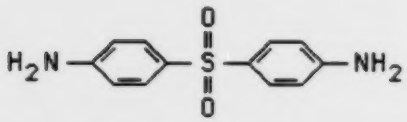
Seven different lots of Narmco 5208 were examined in all. These included five different batches of typical 5208/WC3000 prepreg (Batch Numbers 1010, 1014, 1101, 1103, and 1104), one sample of neat resin coated on a plastic backing sheet (Batch 1047), and one sample of neat resin in bulk form (Batch 1023). Prepreg and reactive resin samples were stored in a freezer at all times except for sampling and performance of experiments.

2.2 FOURIER TRANSFORM INFRARED SPECTROSCOPY

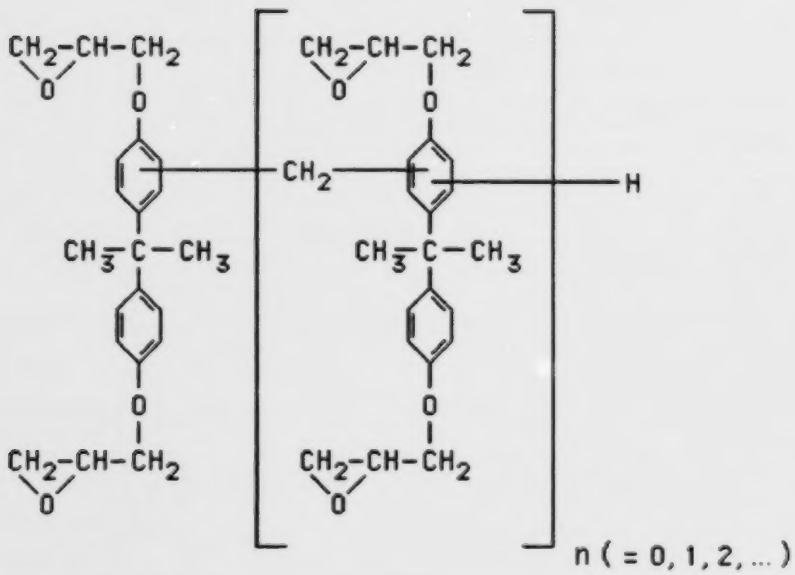
Infrared spectroscopy is one of the most versatile and widely used techniques for the characterization of materials. It is based on the fact that when matter is exposed to infrared radiation it usually absorbs energy at specific frequencies which correspond to the



TGDDM (≈ 69%)



DDS (≈ 22%)



Bisphenol A Novolac Epoxy (≈ 9%)

Figure 1. Chemical structures of principal components of Narmco 5208 resin.

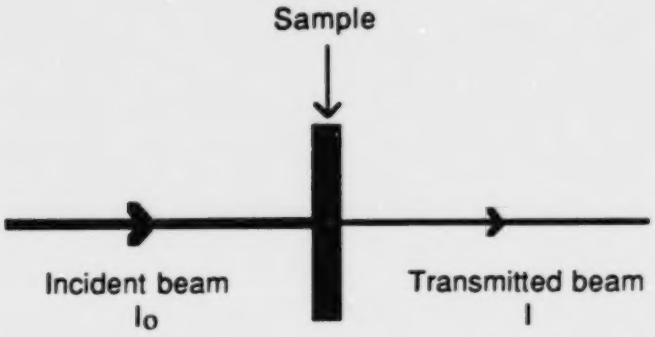
characteristic frequencies of vibration of the atomic groups making up the material. A graph of the degree of absorption versus frequency is known as the infrared spectrum. Often it is quite detailed and serves as a unique "fingerprint" of the material, so IR spectroscopy is widely used for identifying unknown samples. In addition, since the absorption is directly related to the amount of material, it can be used as a quantitative analysis method. It can be applied to solids, liquids, and gases. In the case of composite matrices, it can be used in a number of ways, for example: qualitative and quantitative analysis of the resin, study of the curing reaction, and study of environmental degradation. Several examples are cited in the literature review previously mentioned [1]. The last ten years have seen a tremendous growth in the use of Fourier transform infrared (FT-IR) spectrometers. These instruments, which make use of interferometers rather than monochromators to analyse the frequency distribution of the radiation, are extremely powerful. Compared to conventional instruments they are much more sensitive, rapid, and precise, and the incorporation of a computer makes it possible to extract much more information from the spectrum. The high sensitivity makes it possible to successfully use a number of reflection methods, thereby extending the range of applications to a greater number of materials. A good review, covering both principles and applications, has been published recently [7].

In this project, research was performed with the aim of better understanding the factors which influence the infrared spectra of composite materials, in order to develop more fully its potential. Three different methods of obtaining the spectrum were investigated: transmission, internal reflection (also known as attenuated total reflection), and diffuse reflection. The advantages and disadvantages of all three were compared for both qualitative and quantitative analysis. Spectra were measured using a Nicolet Instruments Model 170SX Fourier transform spectrometer equipped with a wide-range liquid-nitrogen-cooled mercury cadmium telluride detector. Each spectrum corresponded to an accumulation of 128 scans requiring about 80 seconds. The resolution was 4 cm^{-1} and Happ-Genzel apodization was used. A summary of the most important results follows. Full details are given in an earlier report [2].

2.2.1 Transmission

This is the traditional, most widely used method of measuring infrared spectra, particularly for quantitative analysis. As illustrated below, the IR beam is allowed to pass through the sample and the intensity I of the transmitted radiation is divided by that of the incident radiation I_0 to obtain the transmittance T. The graph of T versus frequency is the IR spectrum. Frequency is usually expressed in terms of the wavenumber, or the reciprocal of the wavelength, with units of cm^{-1}. For many purposes, including quantitative analysis, the transmittance must be converted to absorbance A using the

equation $A = -\log_{10}T$. According to the Lambert Absorption Law, the absorbance is directly proportional to the absorption coefficient α, which is an intrinsic property of the material being examined, and to the sample thickness.



A typical sample of carbon-epoxy prepreg could not be measured directly in transmission because it would absorb practically all the incident radiation. To obtain a good spectrum of the resin, it is necessary to extract it from the prepreg with a solvent and cast a thin film on a window made from IR-transparent material such as potassium bromide (KBr). Of various solvents tested, acetone was found to be the best for Narmco 5208. Since it is difficult to determine the thickness of the film, the amount of sample absorbing is unknown. For quantitative work, this problem is overcome by using one peak in the spectrum as an "internal standard" or reference to which other peaks are compared.

Figure 2a shows the transmission spectrum (converted to absorbance and baseline-corrected) of a thin film of Narmco 5208 resin obtained as just described. The assignment of the peaks is discussed in the earlier report [2]. For quantitative analysis, either peak height or peak area can be used as a measure of intensity. With non-computerized instruments, peak heights are easier to determine. With computerized instruments, peak areas are easily calculated and are believed to be a better indicator of intensity because any variations in band width which may occur are expected to affect the peak area less than the peak height. The bands of greatest interest for quantitative analysis are shown in detail in Figure 3. The first is the aromatic ring band at 1517 cm^{-1}, which arises mainly from the major epoxy; small contributions from the hardener and the minor epoxy are responsible for the shoulder around 1500 cm^{-1}. This band is the most suitable for use as an "internal standard". The second band of interest is really a group of bands at 1146, 1105, and 1073 cm^{-1} arising from the hardener. They are related to the sulphone group, which is not destroyed in the curing reaction, so they do not disappear on curing. The ratio of their area

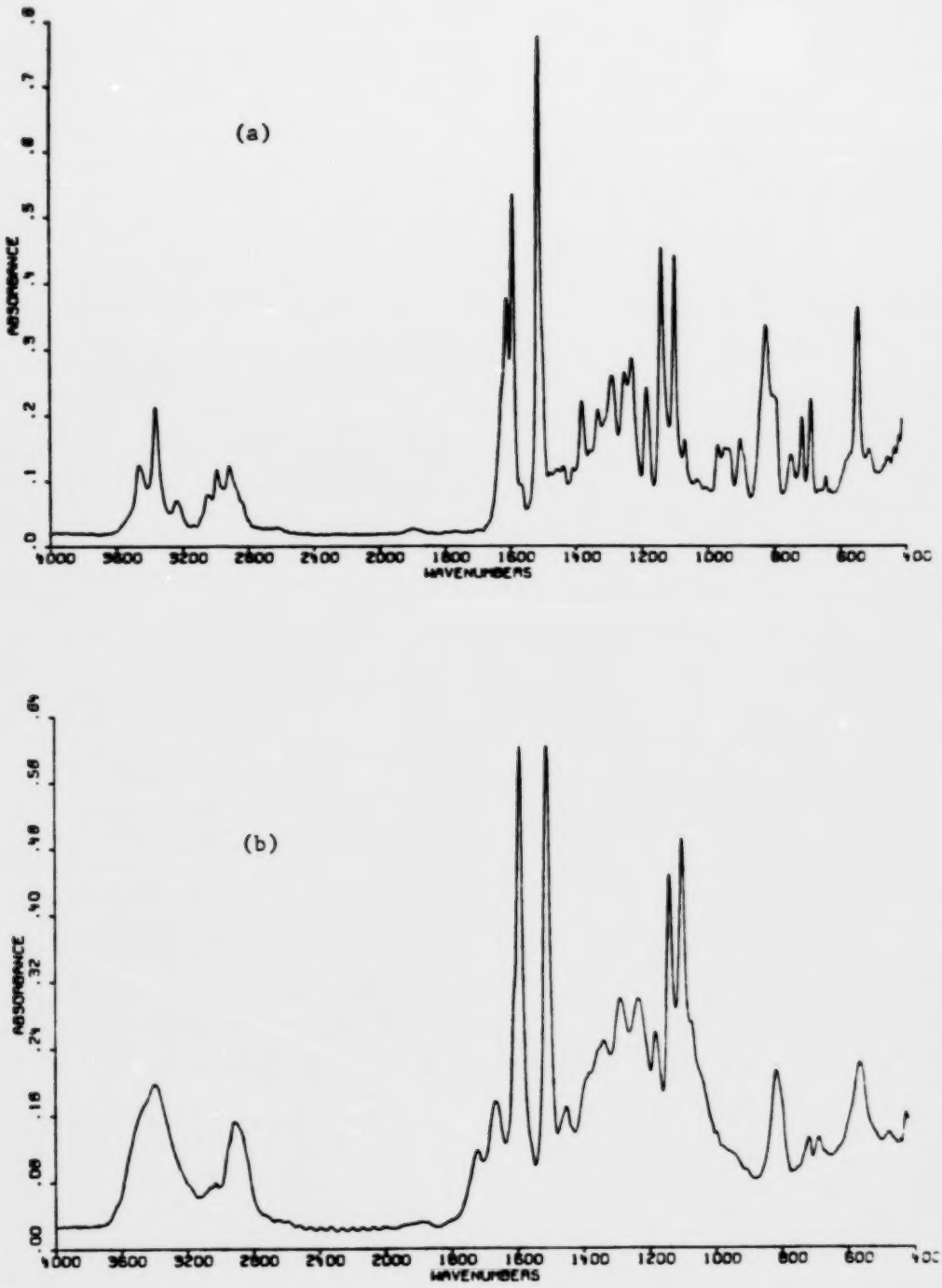


Figure 2. FT-IR transmission spectra of a thin film of Narmco 5208 resin: (a) uncured; (b) cured.

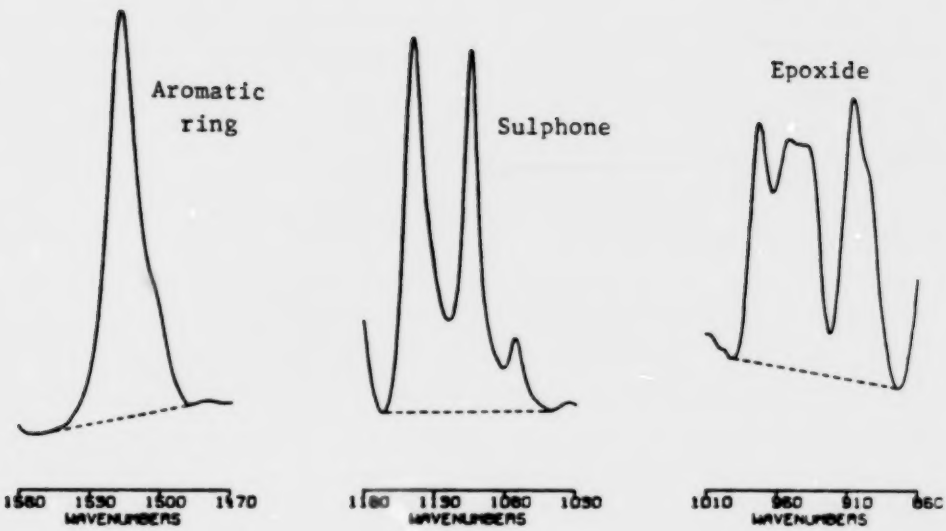


Figure 3. Peaks used for quantitative analysis of Narmco 5208 resin.

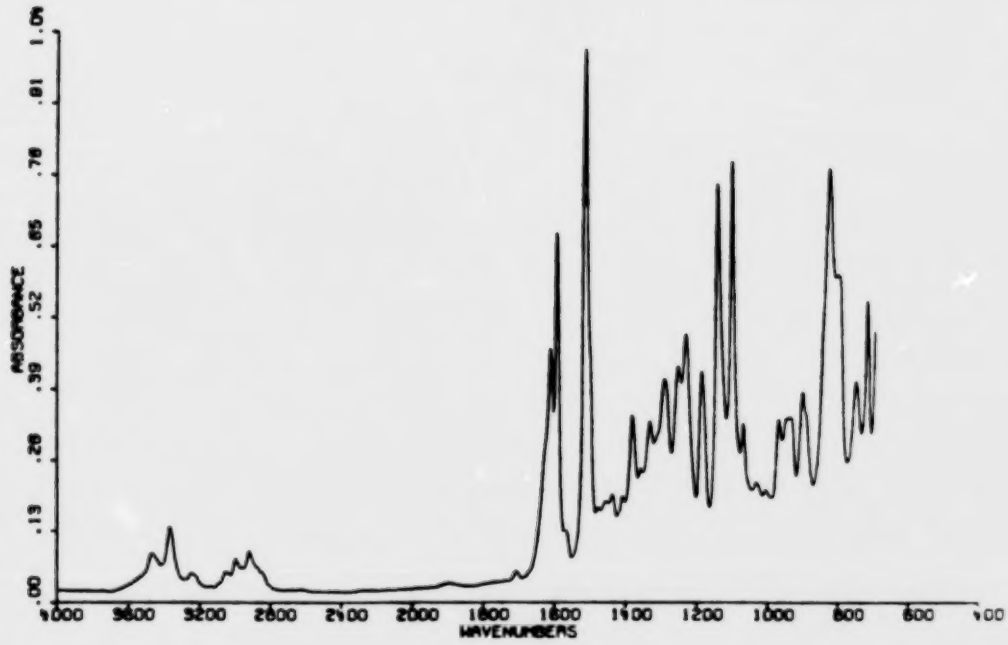


Figure 4. FT-IR attenuated total reflection spectrum of Narmco 5208/WC3000 prepreg (45° Ge prism).

to that of the internal standard is thus an indicator of the total amount of hardener in the system, either free or crosslinked. The third group of peaks of interest occurs between 1000 and 900 cm^{-1} and arises from unreacted epoxy rings. These peaks disappear when the epoxy rings react on curing, so they are an indicator of the amount of unreacted epoxy in the system. Peak areas are calculated by means of appropriate software using the baselines shown in Figure 3. The quantities calculated by taking the ratio of the area (or height) of a given peak against that of the "internal standard" peak are henceforth referred to by the term "index" (sulphone index, epoxide index). It must be emphasized that these indices are somewhat empirical. Band shapes and intensities are affected to some extent by the molecular environment of the absorbing group. They may change, for instance, as the degree of advancement changes through aging or curing. Also, since the internal standard band contains contributions from all three components of the resin, it will be influenced to some extent by variations in composition. Thus the calculated indices are not an absolute measure of the quantity of material involved, that is, they are not necessarily directly proportional. Nevertheless, they are a very good indicator. Any increase in the hardener/epoxy ratio should result in an increase in the sulphone index. Likewise, any decrease in the number of unreacted epoxide groups will be reflected in a decrease in the epoxide index.

When trials were done to determine the reproducibility of quantitative measurements by transmission, it was found that large errors (as high as 28% relative standard deviation) resulted if great care was not taken to prepare films of uniform thickness. The importance of this does not appear to be widely recognized in previous work on analysis of epoxy resins. This may explain why some workers in the field consider infrared spectroscopy to be, at best, only a semi-quantitative tool. We have demonstrated that if this problem is recognized and proper technique is used, the standard deviation can be reduced to the more acceptable level of 2.5% or less.

The method which we recommend, based on these observations, is given in the Appendix. When the seven different lots of Narmco 5208 described in Section 2.1 were analyzed by this procedure, the results given in Table 1 were obtained. Each result is an average over five specimens, with the standard deviation shown in parentheses. In most cases the relative deviation is under 1%. Comparison of the different batches shows that the variation is not particularly large. The sulphone indices are all within ± 4% of the mean (1.056), and the epoxide indices are all within ± 6% of the mean (0.390).

The IR spectrum undergoes substantial changes when the resin is cured. Figure 2b shows the spectrum of a thin film of resin cured between two KBr windows for two hours at 135°C followed by three hours at 177°C. Comparison with Figure 2a shows several changes, of which the most significant is the almost complete disappearance of the epoxy peaks in the 1000-900 cm^{-1} region. By curing the resin in a heatable cell and measuring the

spectrum at regular intervals, it is possible to draw a curve showing the evolution of the epoxide index during the curing process [2]. Another change observable in Figure 2b is the appearance of two new peaks at 1722 and 1667 cm^{-1}. These are due to carbonyl groups formed through oxidation of the resin.

Table 1. Quantitative analysis of different batches of Narmco 5208 by FT-IR transmission spectroscopy. Standard deviations are given in parentheses.

Batch No.	Index = Band area divided by area of aromatic reference band	
	Sulphone index	Epoxy index
1010	1.047 (0.011)	0.391 (0.005)
1014	1.052 (0.005)	0.408 (0.002)
1101	1.022 (0.007)	0.395 (0.002)
1103	1.045 (0.007)	0.375 (0.001)
1104	1.037 (0.008)	0.380 (0.002)
1047	1.087 (0.015)	0.411 (0.007)
1023	1.099 (0.012)	0.370 (0.004)

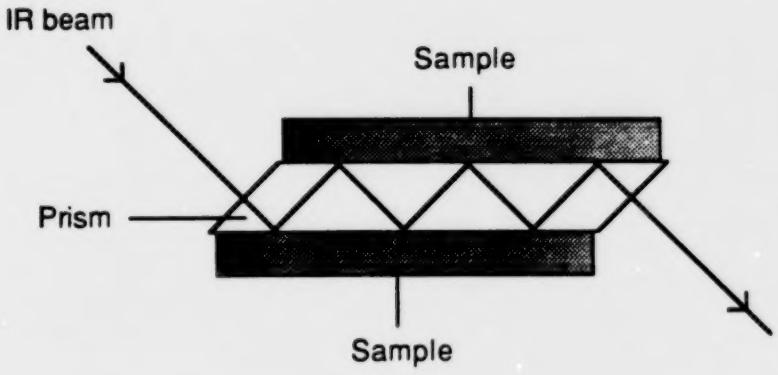
The near-infrared region is also of interest for the characterization of Narmco 5208, especially since it allows the possibility of using fibre optics for nondestructive analysis. Epoxide rings give a peak at 4524 cm^{-1} which disappears on curing. Moisture present in the resin absorbs at 5213 cm^{-1}.

It can be seen that the infrared spectrum can serve a number of useful purposes:

- As a "fingerprint" of the resin it can be used to detect contamination (new peaks) or significant changes in the resin composition.
- The sulphone bands at 1146 and 1105 cm^{-1} can be used to quantify the total hardener content of the resin.
- The epoxide bands in the 1000-900 cm^{-1} region or in the near-infrared at 4524 cm^{-1} can be used to quantify the content of unreacted epoxy, to follow the curing of the resin, and to confirm completeness of cure.
- The appearance of carbonyl bands near 1722 and 1666 cm^{-1} can be used to detect degradation due to oxidation.
- Moisture can be monitored in the near-infrared at 5213 cm^{-1}.

2.2.2 Attenuated Total Reflection

Attenuated total reflection (ATR) spectroscopy, also known as multiple internal reflection (MIR), has been described in depth by Harrick [8]. The method is widely used for studying the surface of solid samples, and is also being used more and more for highly absorbing liquids and for "on-line" measurement in industrial processes. The principle is illustrated in the following diagram:



The sample is placed in intimate contact (using pressure if necessary) with an infrared-transmitting prism whose index of refraction is higher than that of the sample. Commonly used prism materials are KRS-5 (thallium bromoiodide) and germanium. As the beam passes through the prism it is reflected several times at the prism-sample interface. The angle of incidence is usually 45° or 60°. When an absorbing sample is in contact with the prism, the IR beam is "attenuated" by a partial absorption of the evanescent wave existing at the prism/sample interface. Before applying the sample to the prism, a "background" spectrum is recorded for the prism alone. The spectrum is then measured with the sample present, and ratioed against this background to give the spectrum of the sample. The exact nature of this spectrum depends on a number of factors such as angle of incidence, indices of refraction of both prism and sample, number of reflections occurring in the prism, and degree of contact between sample and prism. As a result, there are two important differences between ATR and transmission spectra. Firstly, in addition to the absorption coefficient α of the sample, the index of refraction n can affect the spectrum and cause apparent peak distortions. Secondly, even if refractive index effects are negligible, in ATR the effective sample penetration depth is proportional to the IR wavelength. As a result, ATR spectra appear "skewed" when compared to transmission spectra, with peaks at shorter wavelength (higher wavenumber) appearing less intense. This can be corrected

mathematically. Under typical conditions, the effective penetration depth, as defined by Harrick [8], is of the order of magnitude of one micrometre.

The ATR method is particularly interesting for prepreg analysis because it is possible to measure the IR spectrum directly from the prepreg, without performing the solvent extraction step needed for transmission analysis. The prepreg is simply cut with scissors to give two strips of the appropriate size (about 5 x 1 cm), which are placed in contact with the prism in the ATR accessory. Usually, tightening the clamp screw with finger pressure gives good enough contact to obtain a suitable spectrum of the layer of resin on the surface. Unfortunately, cured composites are difficult to measure in this way because in order to achieve good contact, considerable pressure must be applied, and this can ruin the prism. The work reported here was done using a Twin Parallel Mirror Reflection Attachment (Variable Angle Manual) from Harrick Scientific Corp., with Internal Reflection Accessory using single-pass parallelogram prisms (50 x 10 x 3 mm).

A test of different prisms showed that the best results were obtained with a 45° germanium prism, as compared to KRS-5 prisms with angles of 45° or 60°. Because of its higher index of refraction, the germanium prism results in less peak distortion and more reproducible quantitative results.

Because the ATR spectrum is measured with the carbon fibre reinforcement present, it shows an underlying background absorption, particularly at lower wavenumbers, due to absorption and/or scattering by the fibres. The importance of this absorption will vary depending on the thickness of the surface layer of resin. It can be "removed" by baseline correction after the spectrum is converted to absorbance. Such a spectrum, obtained with a 45° Ge prism for a sample of Narmco 5208/WC3000 prepreg, is shown in Figure 4. Comparison with the transmission spectrum of Figure 2a shows the two to be similar but not identical. Firstly, the ATR spectrum shows a small peak at 1708 cm^{-1} which does not appear in the transmission spectrum. This was found to be due to a volatile product which was identified from its IR spectrum as acetone, apparently residual solvent from the prepreg manufacturing process. It is not seen in transmission because acetone is used to extract the resin from the prepreg and is then evaporated, together with any other volatiles present, before the spectrum is recorded. Secondly, compared to the transmission spectrum, the peaks at higher wavenumber appear less intense, because of the effective penetration depth effect mentioned above. If desired, the ATR spectrum can be "normalized" by multiplying by $\nu/1000$, where ν is the frequency in wavenumbers. This gives a spectrum similar to the transmission spectrum.

For quantitative analysis, we have demonstrated that by using suitable conditions results can be obtained with a relative standard deviation of less than 1.5%, which is better than in transmission, even with careful sample preparation. This is because ATR is not

subject to the problem of nonuniform film thickness. A second important advantage is that ATR measures the prepreg as received. Thus, sample preparation is much faster and easier, since solvent extraction and film casting are not required, and ATR can detect the presence of volatile materials such as acetone, which are lost in the transmission method. Hence ATR is recommended over transmission for quantitative analysis of Narmco 5208 prepreg. The optimized method is given in the Appendix.

Six of the seven batches of Narmco 5208 analyzed by transmission were also analyzed by this method. Batch Number 1023 was excluded because it consisted of neat resin. The results are summarized in Table 2. Each result is an average over five specimens, with the standard deviation shown in parentheses. In most cases the deviation is less than 1%.

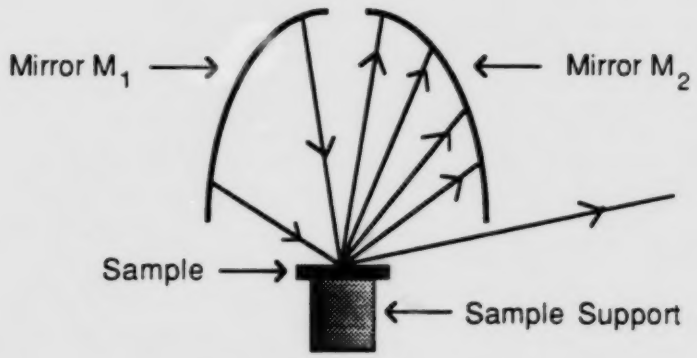
Table 2. Quantitative analysis of different batches of Narmco 5208 by attenuated total reflection FT-IR. Standard deviations are given in parentheses.

Batch No.	Index = Band area divided by area of aromatic reference band	
	Sulphone index	Epoxy index
1010	1.482 (0.006)	0.677 (0.008)
1014	1.486 (0.009)	0.676 (0.006)
1101	1.457 (0.005)	0.688 (0.004)
1103	1.509 (0.004)	0.656 (0.005)
1104	1.468 (0.012)	0.668 (0.015)
1047	1.484 (0.002)	0.694 (0.003)

The calculated indices are considerably different from those obtained in transmission because they are not corrected for the frequency dependence of the sample penetration. If desired, this can be done by multiplying the indices by factors corresponding to the ratio of the frequencies of the two peaks involved, in which case the results are in excellent agreement with those obtained in transmission. As in transmission, comparison of the different batches shows no substantial variations. All sulphone indices lie within ± 2% of the mean (1.481), and all epoxy indices lie within ± 3% of the mean (0.677). These ranges are only about half as wide as observed in transmission, and the reason is not obvious. However, the general trends are much the same.

2.2.3 Diffuse Reflection

Although diffuse reflection (DR) spectroscopy has been known and studied for a long time, it did not come into widespread use in infrared spectroscopy until the highly sensitive FT-IR instruments were developed. Since then it has proved extremely useful in a number of applications [9, 10]. The principle is illustrated in the following diagram:



An elliptical mirror (M_1) focuses the infrared beam onto the surface of the sample, which may be a powder or a rough surface. Part of it is absorbed and the rest is reflected in all directions. A second elliptical mirror (M_2) captures some of this scattered (diffuse) radiation and focuses it toward the infrared detector for analysis. The resulting spectrum is compared to that of a non-absorbing reference such as powdered potassium bromide in order to determine the absorption properties of the sample.

Although generally applied to powders, diffuse reflection can be applied to any surface which reflects diffusely. As a result, it is particularly interesting for the study of composites, because it can be used not only for prepreg but also for cured parts. These are very difficult to measure by attenuated total reflection because it is hard to obtain good contact between the sample and the prism without damaging the prism. In DR, the spectrum can be obtained directly from the surface with no sample preparation other than cutting a piece small enough to fit inside the reflection accessory. With certain types of accessory ("upward-looking" models) even this is not necessary, and large samples can be examined in a nondestructive manner. A few cases have been reported in which the method was used to study curing and degradation in composites [11, 12].

In diffuse reflection, the IR beam usually penetrates the surface of the sample to a depth of several micrometres, and can undergo multiple reflections before leaving the sample and

being detected. Because the physical form of the sample is so different from the transmission case, the Lambert Absorption Law no longer applies. Instead, diffuse reflection spectra are generally analyzed in terms of the following equation, developed by Kubelka and Munk:

$$F(R) = (1 - R)^2/2R = \alpha/s$$

where R is the measured reflectance. Like the absorbance measured in transmission, the Kubelka-Munk function F(R) is directly proportional to the absorption coefficient α, but it also depends on a scattering coefficient s, which varies with frequency. Usually, however, the variation is gradual, and a diffuse reflection spectrum converted to Kubelka-Munk units is very similar, although not identical, to a transmission spectrum converted to absorbance units. Although the Kubelka-Munk equation was derived for the case of a powdered sample, it is sometimes applied to other types of sample for which an appropriate model is lacking.

Unfortunately, diffuse reflection suffers from one important complication, namely front-surface reflection. When the incident infrared beam impinges on the sample surface, part of it is reflected immediately before it ever enters the sample. This reflection is governed by the laws of Fresnel, and depends in a complicated manner on the angle of incidence, the polarisation of the beam, the index of refraction n of the sample, and the absorption coefficient α. The main effect of front-surface reflection is to cause apparent peak distortion as a result of the contribution of the index of refraction. In general, front-surface reflection effects are most pronounced when the sample is strongly absorbing.

The diffuse reflection spectra reported here were obtained using a "Praying Mantis" accessory from Harrick Scientific Corp. Powdered compacted potassium bromide was used as a reference material. The method used is given in the Appendix. Figure 5 shows DR spectra of uncured prepreg and a cured panel made from it. In both cases, the original reflectance spectrum has been converted to Kubelka-Munk units and baseline-corrected to remove the underlying carbon fibre absorption. In the case of the prepreg, all the peaks seen in Figure 5a correspond to those observed in transmission (Figure 2a), except for the peak at 1708 cm^{-1}, which is due to residual acetone left in the prepreg by the solvent impregnation process. This peak is also observed in ATR (Figure 4). For the cured panel (Figure 5b), there are no oxidation peaks at 1722 and 1667 cm^{-1} as were observed in the thin film measured in transmission (Figure 2b), because the panel was cured under vacuum. In addition, the epoxide ring peaks in the 1000-900 cm^{-1} region are somewhat stronger, indicating a lower degree of cure.

Although the DR spectra are of excellent quality and show all the details observed in transmission, some differences can be seen in terms of peak shapes and relative intensities.

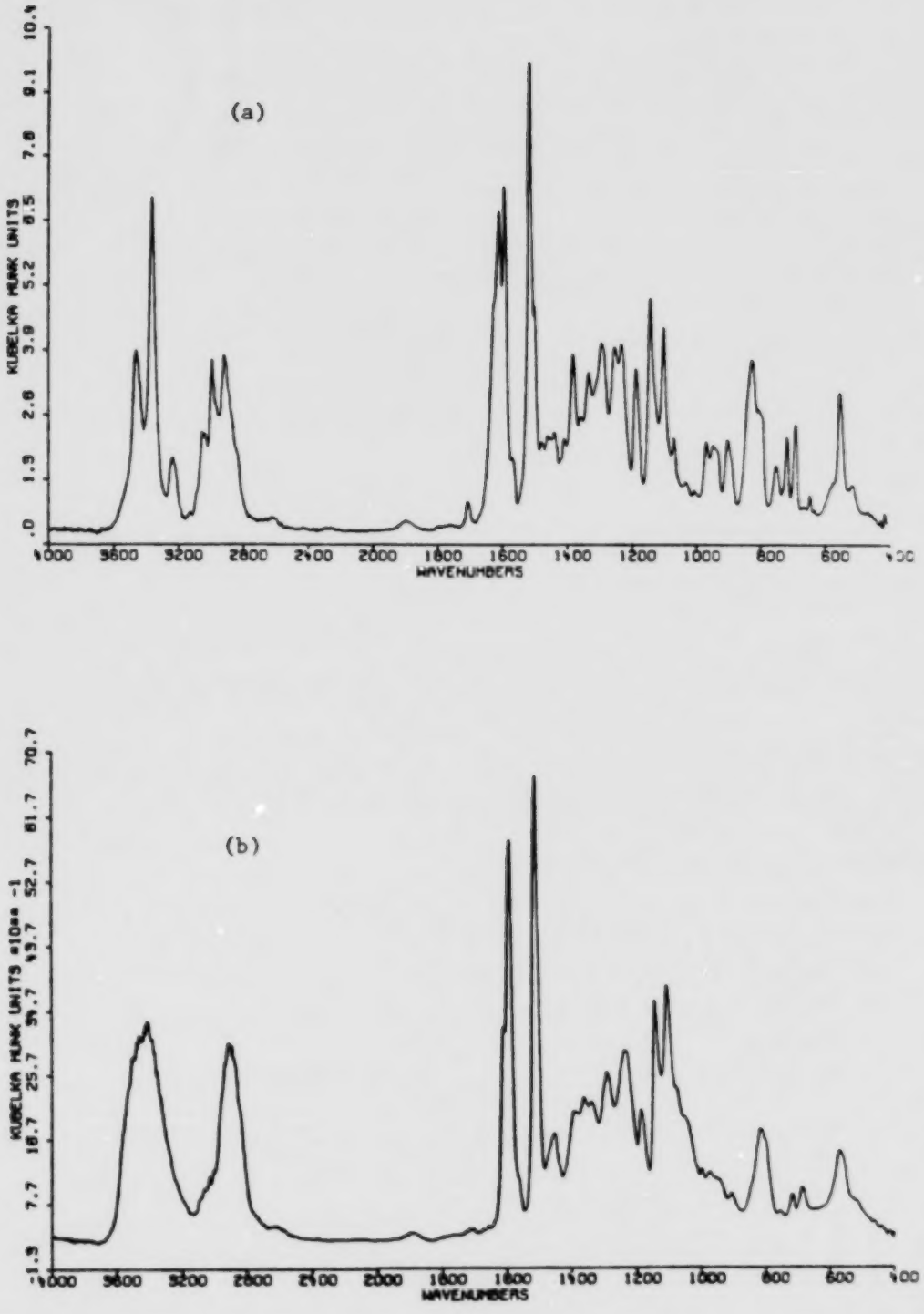


Figure 5. FT-IR diffuse reflection spectra of Narmco 5208/WC3000 composite: (a) prepreg; (b) cured panel.

These may be attributed to contributions by the scattering coefficient s and the front-surface reflection.

As in the case of transmission and ATR, an experiment was done to evaluate the feasibility of using diffuse reflection for quantitative analysis of the prepreg. Although there are complications associated with the technique, it was felt that these might be reproducible enough so that it could still be used, if only in a somewhat more empirical manner than the other methods. If so, it would offer two important advantages: negligible sample preparation and the fact that it can be applied to composites at all stages of cure. Unfortunately, the reproducibility was found to be unacceptably poor, with standard deviations ranging as high as 28%. The main cause appears to be front-surface reflection effects, whose relative contribution varies significantly depending on the thickness of the surface layer of resin. It appears that diffuse reflection is of limited usefulness as a quantitative method for analysis of epoxy-carbon composites. Nevertheless, it can be of great value as a qualitative method for samples such as cured or partially-cured composites, which are difficult to measure by other means.

2.3 HIGH-PERFORMANCE LIQUID CHROMATOGRAPHY

Liquid chromatography (LC) is generally considered to be the most sensitive technique for detecting small variations in the chemical composition of an epoxy resin system. The results which we have obtained support this conclusion [3]. In liquid chromatography [13], the sample is passed through a column containing a stationary solid phase and a mobile liquid phase. The relative affinities of a given compound for the two phases determines the time it takes to pass through the column. Thus the different components of the sample leave the column at different times, and are detected by a suitable device. The chromatogram, or graph of detector signal versus elution time, shows peaks corresponding to the different components of the mixture, and the signal intensity is proportional to the quantity present. This separation of a complex mixture into individual components makes it possible to monitor precisely the overall composition, including the extent of reaction advancement between an epoxy resin and a hardener.

Liquid chromatography can be divided into different classes. In this work, three different techniques were studied, namely reverse-phase liquid chromatography (RPLC), high-speed reverse-phase liquid chromatography (HS-RPLC), and high-performance size-exclusion chromatography (HPSEC). In RPLC, the separation is governed largely by the polarity of the different compounds present, whereas in SEC, the separation is achieved on the basis of molecular size.

2.3.1 Reverse-Phase Liquid Chromatography

Reverse-phase liquid chromatography (RPLC) is currently used in about 80-90% of all the separations done by high-performance liquid chromatography. As opposed to normal-phase liquid chromatography, RPLC makes use of a nonpolar stationary phase with a polar mobile phase or eluent. Usually, the stationary phase is hydrocarbonaceous, the most common groups being octyl (C_8) and octadecyl (C_{18}) alkyl chains. These are bonded to silica particles to convert polar hydroxyl groups to a nonpolar surface. The eluent generally consists of a binary mixture of water with an organic solvent such as acetonitrile, methanol, or tetrahydrofuran. To a first approximation, the retention mechanism of a solute is governed by its polarity in relation to the polarity of the mobile phase. A nonpolar compound is more strongly retained on a nonpolar stationary phase than is a polar compound. Thus, an increase of the organic content of the eluent decreases the polarity of the mobile phase and results in more rapid elution of the solute. Consequently, for a given chromatographic column, a method of separation is optimized by varying the eluent composition in order to obtain the most efficient separation in the shortest time.

In isocratic elution, the eluent composition is not modified during a chromatographic run. In gradient elution, on the other hand, the percentage of organic solvent in the mobile phase is usually increased gradually in order to increase the eluotropic strength and speed up the elution of strongly retained compounds. The main advantage of this technique is that the more rapidly-eluting compounds can be well separated by using a more polar mobile phase at the beginning, and then the more strongly retained compounds can be eluted in a reasonable time by continuously increasing the eluotropic strength of the eluent. Among the disadvantages are the fact that the column must be regenerated to its initial condition after each analysis (a time-consuming procedure), and the detector must be insensitive to the variation of the mobile phase composition. For the analysis of epoxy resins, which contain many compounds with different polarities, gradient elution gives a much more efficient separation.

A considerable amount of experimentation was performed to develop an optimized method for the separation of Narmco 5208 resin. This involved a study of various columns, eluents, gradients, detection wavelengths, and methods of treatment of the data. Full details are given in an earlier report [3]. The work was done on a Varian Model 5000 liquid chromatograph equipped with a Rheodyne Model 7126 automatic universal injector (10 µL) and a Varian Model UV-100 variable wavelength detector with a 4.5 µL flow cell. Chromatograms were recorded on a Varian Vista 401 data station and data were transferred to an Apple II+ computer via an RS-232 interface to perform additional data processing.

The best solvent for extraction of the resin from the prepreg was found to be tetrahydrofuran. It is recommended to filter the extract though a 0.5 µm filter before injection on the chromatographic column.

Conventional reverse-phase liquid chromatography uses columns 15 to 35 cm long packed with particles of 5 or 10 μm diameter, and a typical eluent flow rate of 1.0 mL/min. For Narmco 5208, a test of various such columns showed that the best separation was achieved with either a Varian MCH-5-n-CAP or a Hypersil MOS-1 column, at least 25 cm long. Both contain 5 μm particles with monomeric surface coverage, capped with trimethylsilyl groups. The Hypersil MOS-1 column, which has C_8 alkyl groups, gave somewhat better resolution than the MCH-5-n-CAP column, which has C_{18} groups.

As eluent, various combinations involving acetonitrile (ACN), tetrahydrofuran (THF), methanol, and water were tested. The best results were obtained using a linear gradient based on acetonitrile and water. With a constant flow rate of 1.0 mL/min, the composition is varied from 50/50 H_2O/ACN to 100% ACN over a fifteen-minute period, kept at 100% ACN for a further fifteen minutes, then returned to 50/50 in one minute and kept there for 20 minutes until the column is regenerated.

For full quantification of the results, it is recommended to add acetophenone as an internal standard and to use peak areas rather than heights. The best wavelength for UV detection is 230 nm. Full details of the recommended procedure are given in the Appendix.

Figures 6 and 7 show the chromatograms obtained with the MCH-5-n-CAP and Hypersil MOS-1 columns respectively. The identity of the most important peaks was established by running samples of the individual components present in the resin, by performing Fourier transform infrared spectroscopy on recovered fractions, and by examining chromatograms of prepreg samples which had been partially polymerized by heating at 100°C. They are as follows:

Peak No.	Identity
1	DDS monomer (hardener)
4	ACP = Acetophenone internal standard
7	RP = TGDDM-DDS 1:1 reaction product
9	TGDDM monomer (from major epoxy)
10	DGEBA monomer (from minor epoxy)

For quantitative treatment of the data, two procedures are suggested. The first involves taking the ratios of the areas of peaks 1, 7, and 10 with respect to the area of peak 9, the TGDDM peak. This gives three "indices" which are indicators of the state of the resin. While this may be adequate for routine control purposes, a more complete picture of the resin composition is obtained by using the internal standard and calculating "normalized" peak areas according to the following equation:

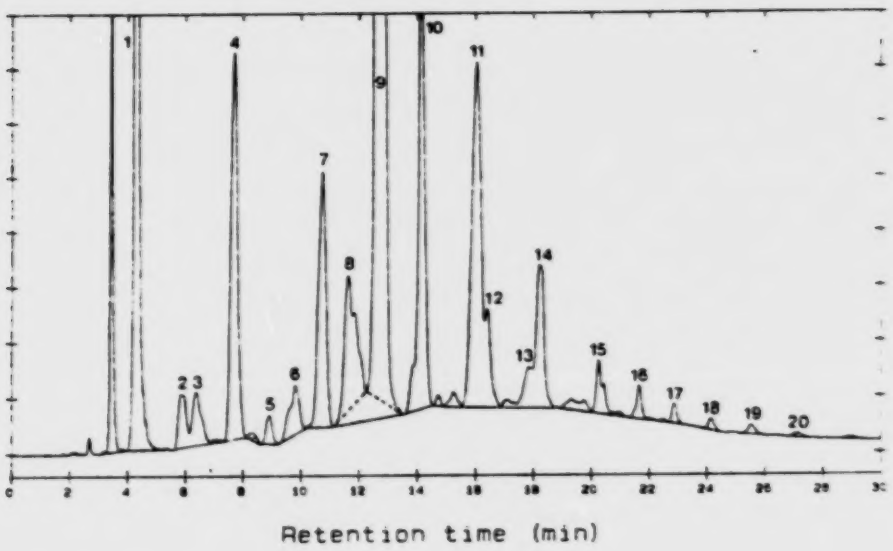


Figure 6. RPLC chromatogram of Narmco 5208 resin obtained using an MCH-5-n-CAP column.

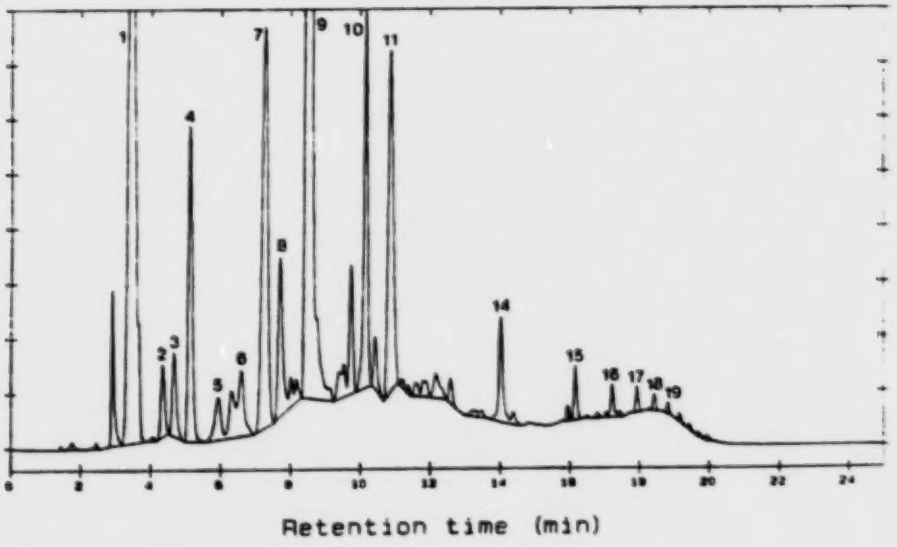


Figure 7. RPLC chromatogram of Narmco 5208 resin obtained using a Hypersil MOS-1 column.

$$\text{Normalized area} = \frac{\text{Peak area}}{\text{Acetophenone peak area}} \times \frac{\text{Wt. acetophenone}}{\text{Wt. of resin}} \times 100$$

This gives quantities in the range of 0.2 to 20 which are directly proportional to the percentage by weight of the compound in question in the resin system.

The seven different lots of Narmco 5208 described in Section 2.1 were analyzed by RPLC according to the method described in the Appendix, using an MCH-5-n-CAP column. For each batch, two solutions or extractions were prepared, except for Batch 1014, which was extracted four times. Each solution was injected three times and the averages of all these values for the main peaks are reported in Table 3, both as normalized values with respect to acetophenone internal standard and as ratios with respect to the TGDDM peak.

Table 3. RPLC results for different batches of the Narmco 5208 system; normalized areas with respect to acetophenone, and area ratios w. r. t. TGDDM

Peak	1103	1101	1104	1010	1014	1047	1023
1 (DDS)	4.810	3.600	4.311	3.719	4.130	4.795	3.034
7 (RP)	1.204	1.742	1.336	1.785	1.623	1.110	2.406
9 (TGDDM)	13.56	12.72	13.19	12.70	13.37	13.54	12.33
10 (DGEBA)	1.879	1.324	1.626	1.185	1.552	0.792	0.709
1/9	0.355	0.283	0.327	0.293	0.309	0.354	0.246
7/9	0.089	0.137	0.101	0.141	0.121	0.082	0.195
10/9	0.139	0.104	0.123	0.093	0.116	0.058	0.057

Appreciable variations can be observed among the different batches. For example, Batch 1047 is the least advanced, with the lowest value for the reaction product (RP) and high values for free TGDDM and DDS. This batch consisted of neat resin coated on a plastic sheet without graphite cloth; it is probably less highly advanced than the usual prepreg samples. However, the content of free DGEBA is abnormally low compared to the other batches, so it appears that this batch is unbalanced with respect to the usual composition. Batch 1023 lies at the other extreme, having the lowest values for free TGDDM, DDS, and DGEBA, and the highest value for the reaction product. This batch also consisted of neat resin, this time in bulk form. It is believed that the sample was

heated to reduce its viscosity for transfer to the container in which it was shipped, and that this caused significant advancement of the resin.

Comparison of the five prepreg samples shows results which are in better agreement. Generally speaking, batches 1010 and 1101 are very similar to each other, while the other three (1014, 1103, and 1104) are also similar to each other but slightly less advanced than the first two. The same trends are evident whether the normalized peak intensities or the peak ratios are used as an indicator. However, the normalized peak intensities provide a more complete picture of the variations in composition.

Comparison of the RPLC results with the FT-IR results is difficult, because the two techniques measure different quantities. For example, the epoxide index measured in FT-IR is an indicator of the global epoxy content, whereas the quantities measured by RPLC are related to specific molecules. In FT-IR, the highest epoxide index is observed for Batch 1047 and the lowest for Batch 1023. This is in agreement with the RPLC results, where these two neat-resin batches lie at the two extremes. For the prepreg samples, however, the correlation is less obvious. This is probably because the overall variation is so low, especially in FT-IR. The RPLC results vary over a greater range, so RPLC appears to be a more sensitive technique for detecting small batch-to-batch differences. FT-IR, on the other hand, is considerably faster, if attenuated total reflection is used, and may be adequate for detecting variations which are significant enough to affect the ultimate properties.

2.3.2 High-Speed Reverse-Phase Liquid Chromatography

High-speed reverse-phase liquid chromatography uses short columns (4 cm long) packed with small particles of 3 μm diameter. With these, the flow rate of the mobile phase can be increased to 2.0 or 3.0 mL/min without a significant decrease of the column efficiency. Thus, the analysis time is considerably shorter than with conventional LC columns, although the resolution is not quite as good. The results reported here were obtained on the same equipment just described except that a Rheodyne Model 7410 automatic loop injector (1 μL loop) was used. The column was a Varian Ultra-fast C_{18}-3, which like MCH-5-n-CAP has an octadecyl bonded phase. The optimum elution conditions were found to be somewhat different from the previous case. Using a flow rate of 2.0 mL/min, the initial eluent 20%/80% ACN/H_2O was increased linearly to 100% ACN over 3 minutes, kept at this composition for two additional minutes, and returned to the initial state within 0.1 minutes.

Figure 8 shows a typical chromatogram obtained for a THF extract of Narmco Rigidite 5208/WC3000 prepreg. The most important feature is the fact that the separation time is

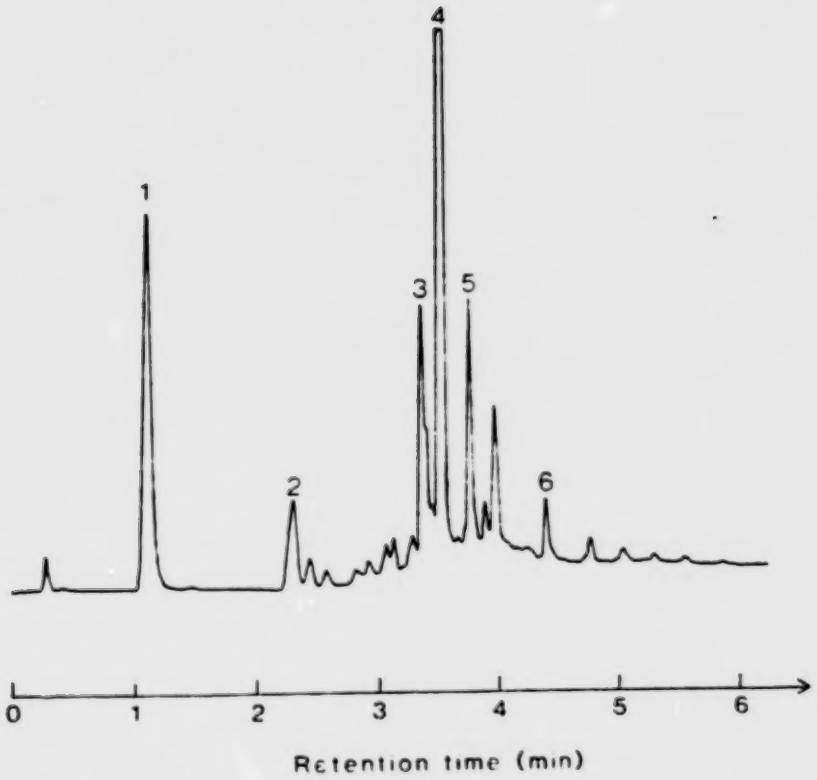


Figure 8. HS-RPLC chromatogram of Nammco 5208 resin obtained using a Varian C_{18}-3 column.

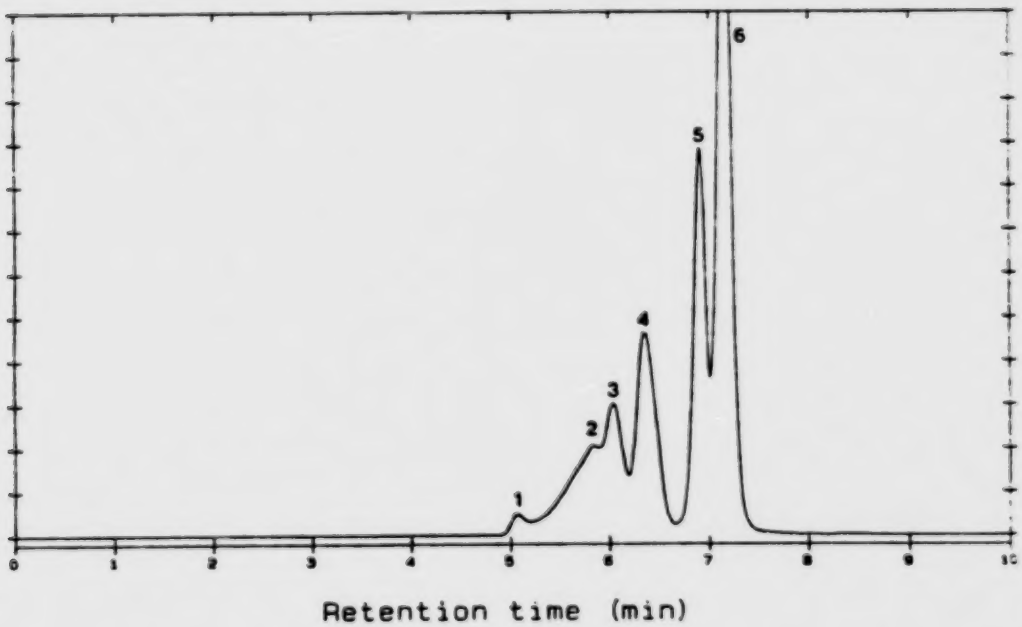


Figure 9. HPSEC chromatogram of Nammco 5208 resin obtained using a PLgel column.

reduced from 25 minutes (see Figures 6 and 7) to 6 minutes. The resolution is almost as good as with the ordinary columns. Peak 1, which is well separated from other major peaks, corresponds to the amine hardener (DDS). Peak 4 corresponds to TGDDM monomer from the major epoxy resin and peak 5 to DGEBA from the minor epoxy (Novolac). Peak 3 is the initial reaction product of TGDDM and DDS. Finally, peak 2 corresponds to acetophenone, which can be added as an internal standard to serve as a reference for quantifying the various peaks of the chromatogram, as described above.

Not only is the separation time reduced with the column containing 3 μm particles, but the column regeneration time is also shorter. It was found that the high-speed columns can be regenerated in 4 minutes, giving a total analysis time of 10 minutes per sample. The ordinary columns require about 30 minutes, for a total analysis time of 60 minutes per sample. Thus, sample throughput is improved by a factor of six with the high-speed columns. Because of this, even though the flow rate is twice as high, there is still a reduction in solvent consumption by a factor of three. These advantages could result in significant savings in a quality control laboratory.

The different batches of Narmco 5208 analyzed by RPLC on ordinary columns were also analyzed by HS-RPLC using the method described in the Appendix. Table 4 gives the results expressed in terms of normalized areas with respect to acetophenone internal standard, and as area ratios with respect to the TGDDM peak. The peak numbering is shown in Figure 8.

Table 4. HS-RPLC results for different batches of the Narmco 5208 system; normalized areas with respect to acetophenone, and area ratios w. r. t. TGDDM

Peak	1103	1101	1104	1010	1014	1047	1023
1 (DDS)	3.292	3.555	3.212	3.241	2.604	4.481	2.737
3 (RP)	3.020	2.862	3.073	3.106	3.314	1.260	4.449
4 (TGDDM)	12.12	12.09	12.19	11.82	11.08	15.81	12.27
5 (DGEBA)	1.364	1.168	1.230	0.926	1.232	0.564	0.606
1/4	0.272	0.294	0.263	0.274	0.235	0.283	0.223
3/4	0.249	0.237	0.252	0.263	0.299	0.080	0.363
5/4	0.112	0.097	0.101	0.078	0.111	0.036	0.049

The trends observed are generally in agreement with those obtained using ordinary columns (Table 3). Batch 1047 is the least advanced, Batch 1023 the most advanced, and the five prepreg batches are very similar. The difference between the actual figures in the two tables may be attributed to the difference in resolution between the two chromatograms, which also means that the baselines are drawn somewhat differently. For instance, the RP figures are generally higher with the high-speed columns, and this is due to the fact that this peak overlaps with another one which contributes to the calculated area. Also, in Table 4, Batch 1014 appears more advanced. This could be due to the fact that these results were obtained at a much later date, and this particular batch may have undergone some aging as a result of several thaw-freeze cycles.

For quantitative analyses over a long time period, it is advisable to consistently use the same type of column, either a long column (25 cm) packed with 5 µm particles, or a short one (4 cm) packed with 3 µm particles. For some applications, the high resolution of a longer column is not needed and HS-RPLC will be more than adequate for controlling the quality of a product.

2.3.3 High-Performance Size-Exclusion Chromatography

Size-exclusion chromatography (SEC) is a liquid chromatographic technique which separates molecules according to their size. It is sometimes referred to as "gel permeation chromatography". High-performance size-exclusion chromatography (HPSEC) has been defined [14] as "a system in which the number of theoretical plates generated per second is about tenfold greater than that of traditional SEC systems. This means that separations commonly will take 10-20 minutes compared to the much longer (hours) separations of conventional size-exclusion chromatography." This improvement was made possible through the use of highly crosslinked poly(styrene/divinylbenzene) macroporous particles. With 5 µm particles, an epoxy resin separation can be done with a single column rather than the four or five columns usually required in SEC. The resolution on a SEC column is not as good as that obtained in HPLC. However, information on the molecular weight distribution can be useful and the SEC method can be an alternative or a complement to the HPLC method for quality control of a prepreg.

In SEC, the optimization of a separation is relatively easy to accomplish as compared to HPLC because the mobile phase usually consists of a single component, typically tetrahydrofuran or chloroform. The HPSEC results reported here were obtained using a conventional liquid chromatograph (Perkin-Elmer Series 3B with a Rheodyne Model 7125 manual universal injector, 10 µL loop) and a single column (PLgel, 30 cm long x 7.5 mm i.d., 5 µm particles, from Polymer Laboratories). The eluent was tetrahydrofuran with a flow rate of 1.0 mL/min, and the detector was a Varian variable wavelength UV detector,

Model UV-100, set at 254 nm. The method is described in the Appendix. It provides excellent results in a shorter time than conventional SEC methods using several columns.

Figure 9 shows the chromatogram of a THF extract of Narmco 5208 epoxy prepreg, Batch 1103. The separation is achieved in less than 7.5 minutes with good resolution. Comparison with the chromatograms of the individual components [3] showed that peak 5 (at 6.9 minutes) corresponds mainly to DDS and peak 6 (at 7.2 minutes) to TGDDM monomer. It would be expected that the TGDDM would be eluted before the DDS, because the molecular weight is higher, but the "effective molecular size" of the DDS is increased through strong hydrogen bonding with the THF eluent. Peak 1 arises from a component of the minor epoxy, whereas peaks 2, 3, and 4 correspond to oligomers present in the major epoxy and to products formed by reaction between DDS and epoxy.

The different batches of Narmco 5208 previously described were analyzed by HPSEC using THF extracts or solutions. The relative peak areas (expressed as a percent of the total area) are given in Table 5. They correspond to an average over three injections. In addition, the last row of the table shows a "degree of polymerization index" obtained by dividing the total area of the first four peaks, corresponding to molecules of higher molecular weight, by the sum of the areas of peaks 5 and 6, which correspond mainly to monomers. Unlike the case of RPLC, the relative area in HPSEC can be evaluated with high precision because the baseline is quite stable. Also, as there are only 5 or 6 peaks, the computation of data is simpler and more reproducible. The relative standard deviation is generally lower than 1% and often lower than 0.5%. The addition of an internal standard is less important because each peak usually corresponds to several compounds and thus, a variation of the peak area may reflect a variation in composition involving more than one compound.

Table 5. Relative peak areas for HPSEC analysis of different batches of the Narmco 5208 epoxy resin system.

Peak	1103	1101	1104	1010	1014	1047	1023
1 (Novolac)	1.38	0.96	1.13	0.78	1.16	0.39	1.09
2+3	22.07	17.92	19.70	15.20	20.38	8.88	18.84
4	16.73	16.23	16.31	19.26	18.73	16.07	18.69
5 (DDS)	20.74	22.80	21.37	23.87	20.60	25.30	18.49
6 (TGDDM)	38.98	42.04	41.46	40.82	39.06	49.15	42.76
(1 to 4) + (5+6)	0.673	0.541	0.591	0.545	0.675	0.340	0.631

As observed in RPLC and FT-IR, Batch 1047 is the least polymerized of the samples tested. It has the highest values for free TGDDM and DDS and the lowest "degree of polymerization index". Also, the unusually low value for peak 1 indicates a low content of Novolac epoxy. The other batches do not show any substantial variations. Based on the "DP index", the degree of advancement would appear to vary in the order: 1014 ≈ 1103 > 1023 > 1104 > 1101 ≈ 1010 > 1047. Comparison of the HPSEC data with the RPLC results (Tables 3 and 4) shows that the order is not the same for the two methods. This is due to the fact that the HPSEC peaks correspond to the superposition of many molecules at the same retention time, whereas the RPLC peaks correspond to individual molecules such as the TGDDM-DDS reaction product. This makes the HPSEC results more difficult to interpret and generally means that HPSEC is less sensitive to variations in composition than is RPLC. Nevertheless, the HPSEC results corroborate the RPLC results to a certain extent. For example, both show that Batches 1010 and 1101 are very similar, as are batches 1014 and 1103.

When a sample of prepreg from Batch 1014 was heated for four hours at 100°C, the "DP index" increased by 67%.

To summarize, high-performance size-exclusion chromatography with a PLgel column allows rapid analysis of Narmco 5208 resin in less than 8 minutes. Although the technique is not as sensitive as RPLC for detecting variations among different batches, it can be useful for following variations in a given batch, such as changes in the degree of advancement.

2.4 THERMAL ANALYSIS

Thermal analysis [15, 16] is the study of the behaviour of a material when it is subjected to controlled temperature conditions. Usually the temperature is either maintained constant (isothermal conditions) or programmed to increase linearly with time (dynamic conditions). Various methods are used to monitor the material's behaviour. In differential scanning calorimetry (DSC), the quantity measured is the amount of heat released or absorbed by the sample; the data provide information on phenomena such as chemical reactions, phase changes, glass transitions, and crystallization. Thermogravimetric analysis (TGA) monitors the weight of the sample, and is generally used to obtain information concerning thermal decomposition. Dynamic mechanical analysis (DMA) measures the mechanical (stress-strain) response, which is related to chemical and physical changes occurring in the material. In this work, only DSC and TGA were used.

DSC analyses were done using a SETARAM Model CDP111 apparatus. A sample of Narmco 5208/WC3000 prepreg weighing about 40 mg (about 3 x 15 mm in size) is put in a platinum crucible and a DSC curve is recorded at a heating rate of 5°C/min with nitrogen as the atmosphere. Baseline variation is minimized by using a crucible of similar weight as reference. An even better result is obtained if this crucible contains a sample of completely polymerized prepreg of approximately the same weight as the sample being analyzed. Nitrogen is used as atmosphere in order to minimize resin degradation, which tends to become important above about 280°C. A typical DSC curve is shown in Figure 10. A single exothermic peak is observed with a maximum around 250°C. This peak corresponds to the heat evolved by the epoxy curing reaction, and its area (calculated with respect to a baseline drawn between about 130 and 273°C) can be used to determine the exact amount of heat evolved. Dividing this by the weight of resin present gives the specific enthalpy of curing ΔH, which is closely related to the number of unreacted epoxide groups in the resin. Thus it depends on the initial chemical composition of the resin as well as its degree of polymerization, and can be used as a quality control parameter. However, in order to obtain reliable results, the weight of resin in the prepreg specimen analyzed must be accurately known. The nominal resin content of the prepreg studied is 42%, but because the distribution throughout the carbon-fibre cloth is not entirely uniform, the percentage of resin in the small specimens used for DSC analysis may differ from this amount. Consequently, it should be determined for each individual specimen. To do this, a thermogravimetric method was developed. The same specimen used for DSC is transferred to the TGA apparatus (SETARAM Model B70 in the present case) and decomposed by heating at 10°C/min under an oxygen atmosphere. A typical curve is shown in Figure 11. The inflection point occurring near 600°C corresponds to the end of oxidation of the epoxy resin and the beginning of oxidation of the carbon fibres. Its position can be used to determine the true weight of resin in the specimen analyzed and thus calculate an accurate value for ΔH. It was found that values calculated using the weight determined by TGA were much more reproducible than those calculated using the nominal resin content of 42%. For the most accurate results, the small weight loss which occurs during the DSC experiment should also be taken into account.

The recommended thermal analysis method is given in the Appendix, while full details of its development are given in an earlier report [4]. It was used to analyze the different batches of Narmco 5208 described previously. For each batch, two or three specimens were analyzed, and the results are given in Table 6. It is seen that the percentage of resin varies significantly, from 40 to 47%. However, the values of ΔH for a given batch are in excellent agreement (generally less than 2% difference). There is very little variation in ΔH among the different batches. The somewhat higher value for Batch 1047 suggests that this batch has a lower initial degree of polymerization than the others. On the other hand, Batch 1103 has a somewhat low ΔH. These results are in keeping with those obtained by

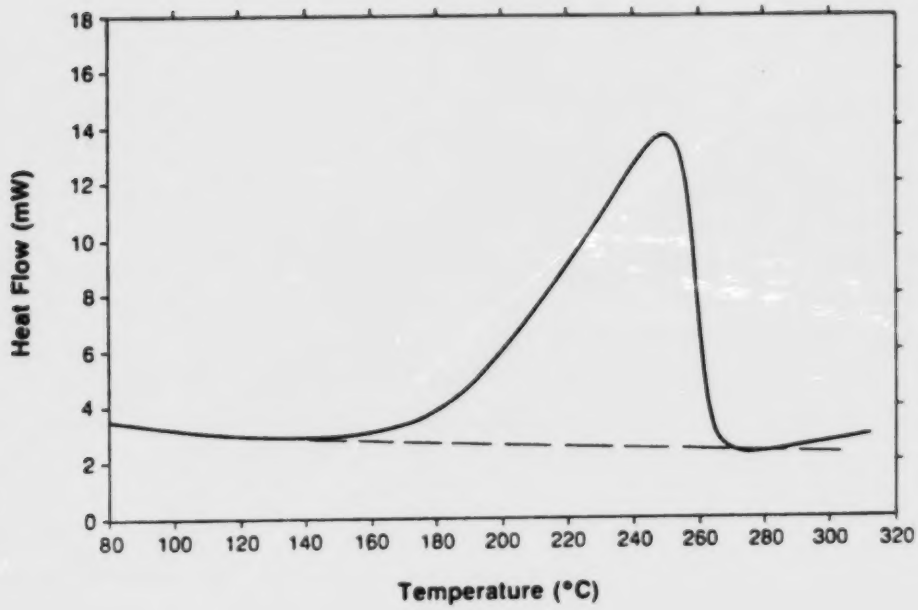


Figure 10. DSC curve obtained for Narmco 5208/WC3000 prepreg.

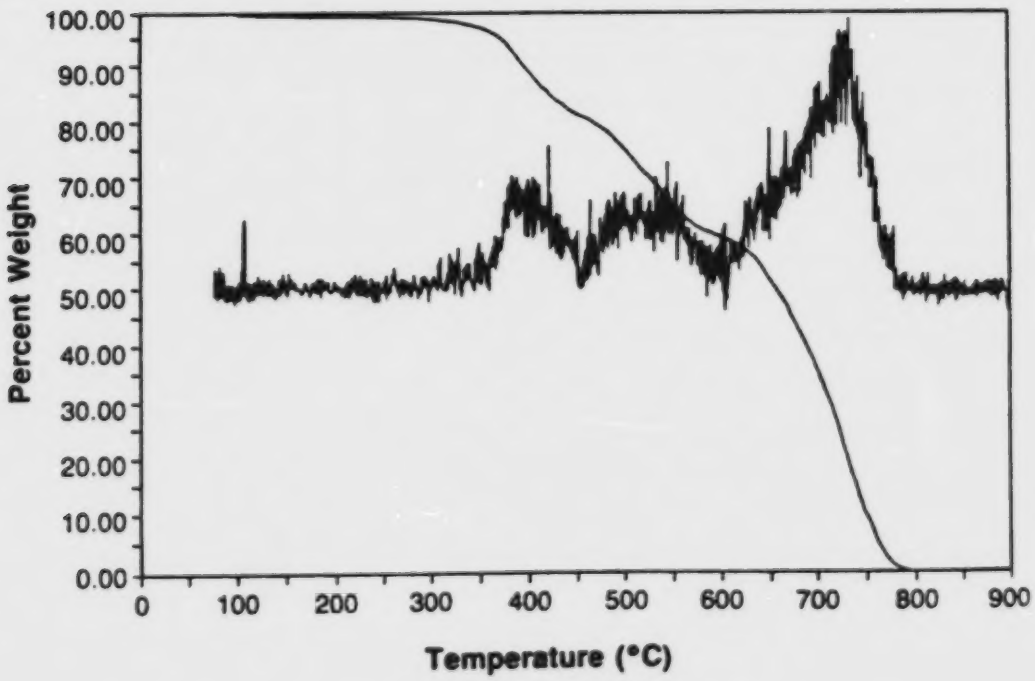


Figure 11. TGA curve obtained for Narmco 5208/WC3000 prepreg.

attenuated total reflection FT-IR (Table 2). This is not surprising, since in both DSC and ATR, the final result is a global measurement over all molecules containing epoxy groups, whereas in RPLC the degree of polymerization is determined from a specific compound (the TGDDM-DDS reaction product) without taking into consideration the influence of other compounds. The good agreement between DSC and ATR suggests that infrared spectroscopy could possibly be used as a faster method to evaluate the degree of advancement.

Table 6. DSC results for different batches of Narmco 5208/WC3000 prepreg.

Batch	% Resin	ΔH (J/g)
1014	44.6, 40.0, 42.8	548, 552, 545
1103	40.4, 42.0	536, 517
1010	47.0, 42.5	548, 542
1101	43.6, 44.5	546, 555
1104	40.5, 40.1	544, 551
1023	(100.0)	568, 563
1047	(100.0)	620, 612

2.5 PYROLYSIS - GAS CHROMATOGRAPHY

In this technique, a sample is pyrolyzed under controlled high-temperature conditions to give a mixture of decomposition products which is then separated and analyzed by gas chromatography. The resulting chromatogram is usually quite complex and can serve as a "fingerprint" of the sample as well as to give qualitative information concerning the nature of the sample. An important advantage of Py-GC is that it can be used for highly polymerized samples such as cured epoxy resins, which are neither volatile enough to be analyzed by gas chromatography nor soluble enough for liquid chromatography. A disadvantage is that, because of problems with reproducibility of pyrolysis conditions, its use as a quantitative tool has been rather limited. Nevertheless, some experiments were done with the Narmco 5208 system in order to explore the possibilities of this technique, and an optimized method was developed (see Appendix for details). More information is given in an earlier report [4].

Analyses were done using a pulse-mode pyrolyzer (Chemical Data Systems Model 170) coupled to a Model 6000 Varian gas chromatograph. A sample of prepreg (about 1 mg) is put in the centre of an open quartz tube about 20 mm long which is then placed inside a

platinum coil probe. The sample is pyrolyzed at 650°C for 10 seconds, and the degradation products are injected, through an interface maintained at 200°C, onto a capillary gas chromatographic column (DB-17, 30 m x 0.259 mm). The temperature program is as follows: 50°C to 60°C at 2°C/min, then 60°C to 250°C at 10°C/min. The components are detected using a flame ionization detector.

Figure 12a shows the chromatogram obtained for Narmco 5208/WC3000 prepreg. By coupling Py-GC with FT-IR it was established that peak 1 is due to phenol and peak 2 to aniline. The phenol originates from the epoxy resin in the system, whereas the aniline comes from the DDS hardener. The ratio of intensity of the aniline peak to the phenol peak should therefore be related to the hardener/epoxy ratio in the system. To test this, an experiment was done using different prepared mixtures of epoxy and hardener, and a good quantitative relationship was observed between these two parameters. Py-GC could therefore be useful if it were necessary to determine the hardener/epoxy ratio in a sample after it was cured. A second experiment involved a study of prepreg at different stages of resin advancement. It was found that the ratios of certain peaks with respect to the aniline peak (the strongest in the chromatogram) vary with the degree of advancement, but the sensitivity is much lower than that of liquid chromatography or FT-IR, and generally speaking, these methods are preferable to Py-GC except in special cases such as that mentioned above.

2.6 DEVELOPMENT OF SPECIFICATIONS

The establishment of acceptable limits for the batch-to-batch variation of materials such as Narmco 5208 is not an easy task. Generally, these products are accepted for use in critical applications only after extensive long-term testing of actual structures made from material known to be of good quality. The only way to unequivocally establish acceptable limits would be to repeat the test program with a number of "off-spec" batches of known composition and to establish correlations between composition and final properties. Because of the time and cost involved, such studies are extremely rare.

An alternative is to perform short-term mechanical testing of simple specimens made in the laboratory. Experiments of this type, some of which are described in the literature review published earlier [1], have shown that the resin chemistry can undergo substantial variations without significantly affecting the mechanical properties. However, as discussed in the next chapter, it would be very dangerous to extrapolate these results, obtained under small-scale "ideal" conditions, to larger, more complex structures made in a factory environment. The processing behaviour would almost certainly be quite different under these circumstances. Hence, this approach is not of much use.

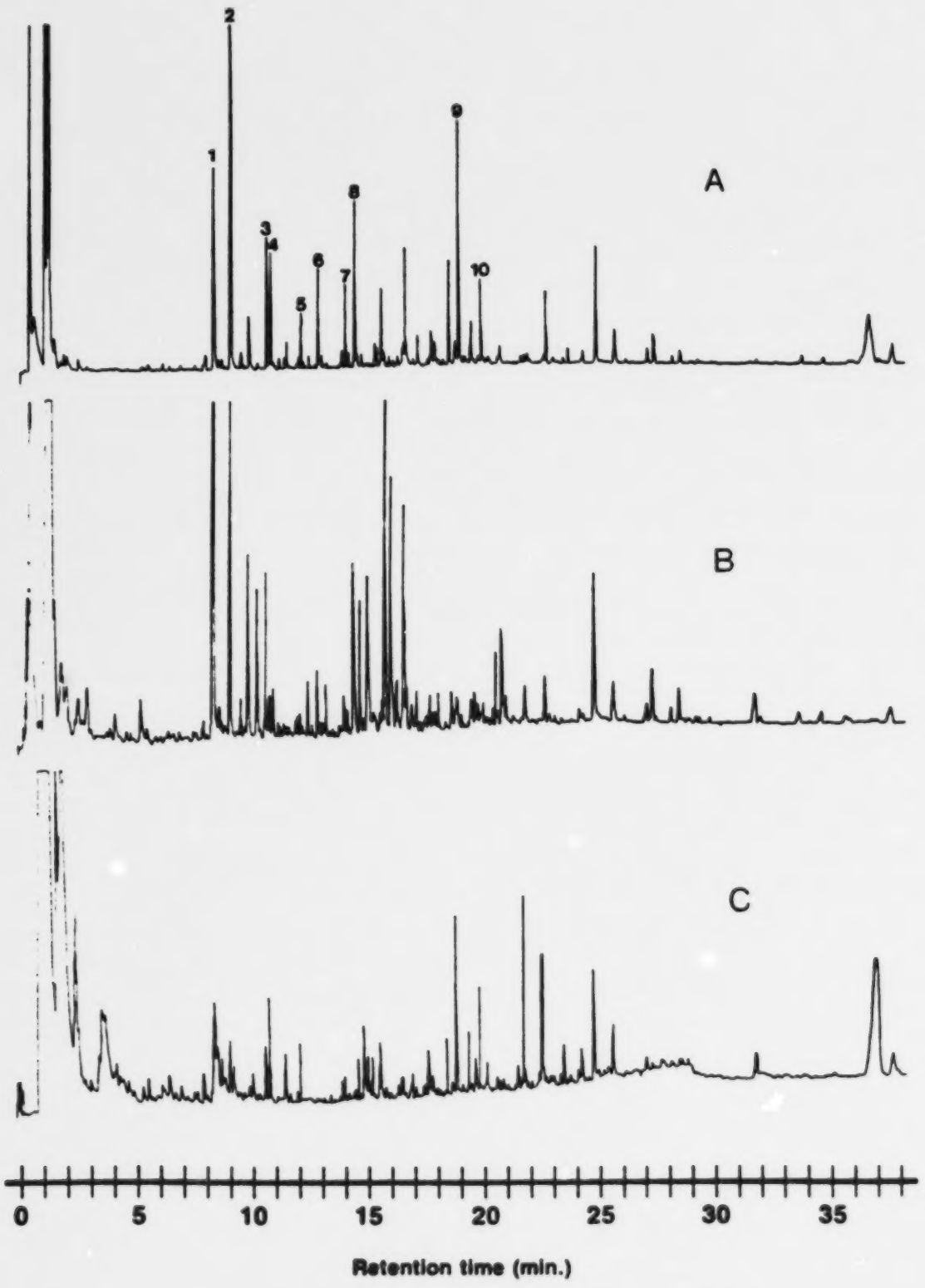


Figure 12. Py-GC chromatograms of (a) Narmco 5208/WC3000 prepreg, (b) Ferropreg CE-9000-2 Kevlar prepreg, and (c) Araldite MY 720 epoxy resin.

The only alternative left is to apply rather arbitrary limits to ensure that batches used for critical applications are reasonably similar to the one(s) used for the qualification test program. These limits can best be established by testing a number of batches over a period of time, possibly with the application of statistical process control methods. Batches which do not meet the specifications would be rejected or used for less critical parts. This approach, while not as scientific as one would like, is nevertheless certain to result in better quality control than the traditional mechanical testing of small specimens.

3. THE AGING OF NARMCO 5208 PREPREG

This chapter describes a particular application of the chemical analysis methods developed for Narmco 5208 as outlined in the previous chapter. Probably the most likely cause of variation in this system is gradual polymerization during handling and storage. Once the prepreg is manufactured, it is a reactive mixture which must be stored at freezer temperatures and protected from humidity. Otherwise, the chemical reactions which occur ("resin advancement") will change the physical properties and processing behaviour of the material. This in turn can affect the mechanical performance of parts made from the prepreg, especially in the long term. It is therefore important to have reliable methods for checking the degree of advancement of the prepreg to ensure that it has not been exposed to adverse shipping and storage conditions. The physicochemical methods described in the previous chapter are particularly useful in this respect.

In order to demonstrate this, a systematic study was undertaken in which sheets from a newly-received shipment of Narmco 5208/WC3000 prepreg were exposed in a controlled atmosphere at 22°C and 50% relative humidity for periods up to 66 days. At selected intervals, sheets were removed and subjected to extensive chemical, physical, and mechanical testing. The aim of the study was to determine the magnitude of the changes which occur, to compare the sensitivity of the different methods for detecting these changes, and to investigate the correlations between physical, chemical, and mechanical properties.

Chemical testing was done as described in the previous chapter. Physical and mechanical testing were done according to Canadair's specifications, which resemble standard ASTM methods. The resin content of the prepreg was determined in three ways: acetone extraction (for FT-IR), tetrahydrofuran extraction (for LC), and thermogravimetric analysis (for DSC). Other physical tests done were volatiles content (ASTM D3530), resin flow (ASTM D3531), and gel time (ASTM D3532). Panels for mechanical testing were prepared by vacuum-bag autoclave curing in a two-stage process (1 hour at 135°C, followed by 2 hours at 177°C). For tensile measurements (ASTM D3039), four plies of prepreg were used, whereas six plies were used for compressive measurements (ASTM D695) and short beam shear strength (ASTM D2344).

The detailed results are given in an earlier report [5]. Figure 13 shows some of the more interesting chemical testing results. The first of these is the epoxy index as measured by FT-IR in transmission; it is directly related to the content of unreacted epoxy groups in the resin. Up to 50 days (filled symbols) it decreases linearly with time at a rate of 0.34% per day, based on the initial value. Thus after 50 days aging, about 17% of the epoxy groups initially present have reacted. A similar result was obtained using attenuated total reflection FT-IR.

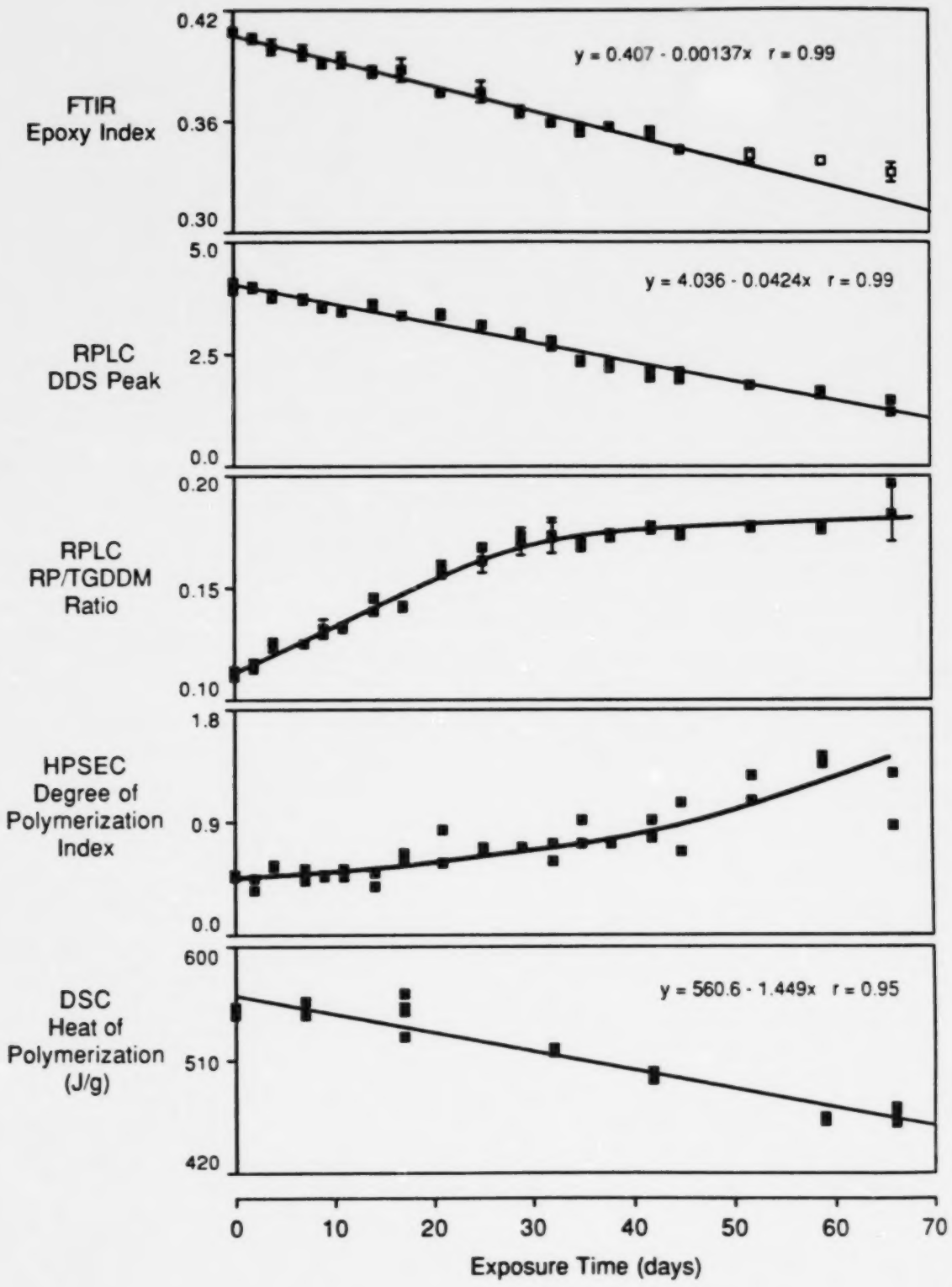


Figure 13. Results of chemical testing of aged Narmco 5208/WC3000 prepreg.

The second graph shows the content of free DDS monomer as determined by reverse-phase liquid chromatography (RPLC). The quantity plotted is the peak area normalized with respect to acetophenone internal standard; it is directly related to the percent by weight of free DDS in the resin. Here too a steady linear decrease is observed, with a rate of 1.02% per day. After 50 days exposure about half the DDS molecules have combined with an epoxy molecule. High-speed RPLC gave similar results.

The third graph, also obtained by RPLC, shows the ratio of the reaction product (RP) peak area to the TGDDM peak area. Over the first thirty days, this ratio increases significantly, as TGDDM disappears and RP is formed. However, after this point it levels off, because less RP is formed (there is less TGDDM and DDS to produce it) but the existing RP undergoes further reaction through its epoxy or amine groups. Again, high-speed RPLC gave similar results.

The fourth graph gives some results from high-performance size-exclusion chromatography (HPSEC). In this case, the quantity plotted is the "degree of polymerization index", obtained by dividing the area of high-molecular-weight peaks by that of low-molecular-weight peaks (chiefly due to TGDDM and DDS monomers). Although the degree of scatter is greater than in FT-IR or RPLC, a steady increase is observed.

Finally, the fifth graph shows the enthalpy of polymerization per unit weight of resin, as determined by DSC and TGA. This is closely related to the number of epoxy groups available for reaction. Again, there is a gradual decrease, of the order of 0.26% per day, similar to that observed for the epoxy index in FT-IR.

Taken together, the graphs given in Figure 13 show that significant chemical changes occur when Narmco 5208 prepreg is exposed at room temperature and 50% R.H., and that these are readily detected by various physicochemical techniques. The effect on the physical and mechanical properties will now be considered.

The physical testing results are summarized in Figure 14. The first graph shows the resin content, as determined by acetone or THF extraction or by thermogravimetric analysis. No significant variation is observed, indicating that even after 66 days the resin has not polymerized to the point where it becomes noticeably insoluble in these solvents. The second graph shows the volatiles content. Here, a substantial drop is observed in the first few days of aging, followed by a levelling off at around 0.8%. IR analysis showed the volatile materials to be water and acetone. The initial drop is attributed to loss of acetone and is accompanied by a noticeable loss of tack in the prepreg. The third property shown is the resin flow, the amount of resin squeezed out of the prepreg when it is heated and pressed under controlled conditions. In spite of the chemical changes occurring in the prepreg, the resin flow is barely affected. This is not the case, however, for the gel time, shown in the fourth graph. This is the time required for the resin to "set" when it is heated

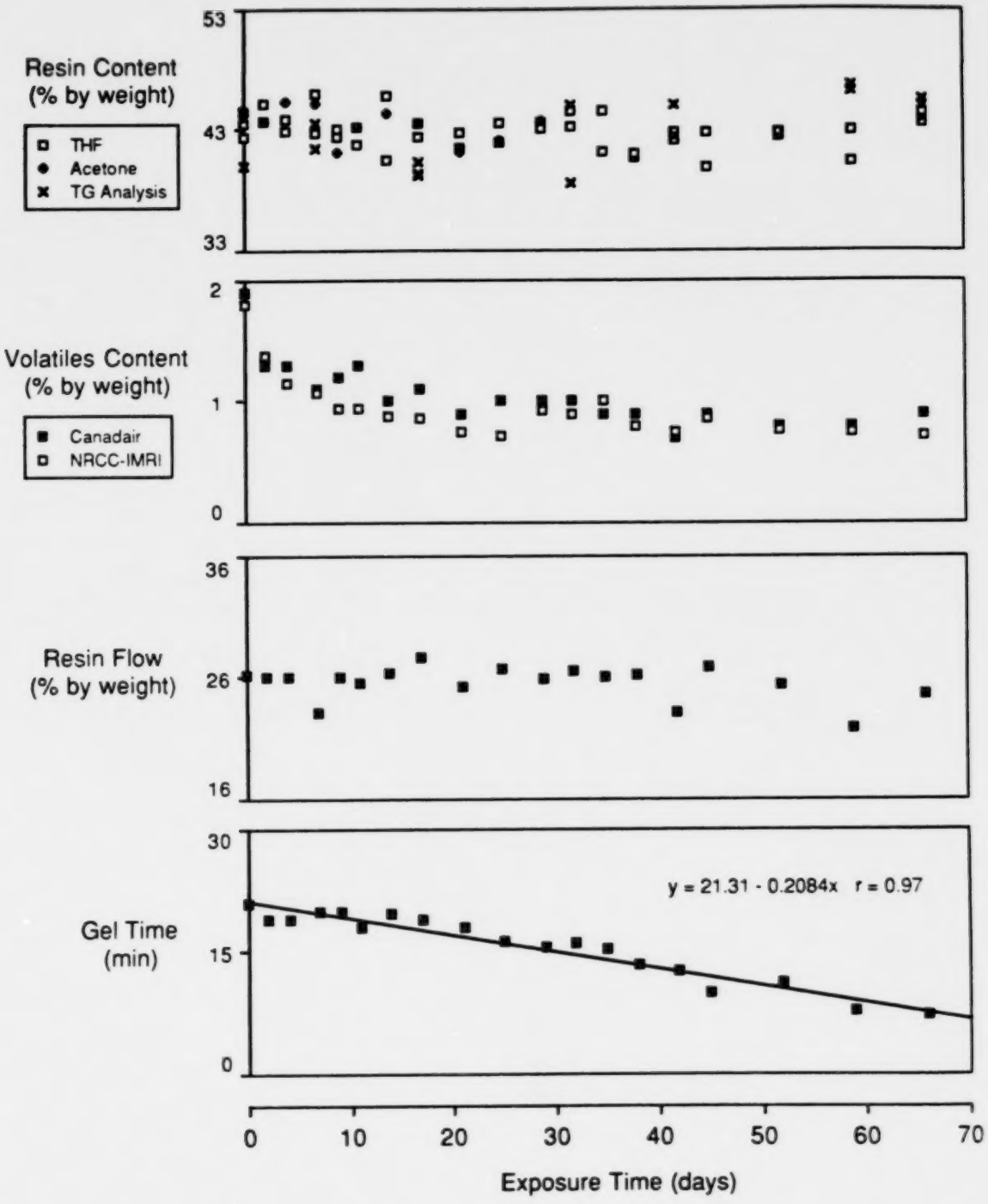


Figure 14. Results of physical testing of aged Narmco 5208/WC3000 prepreg.

at 177°C. Over a 50-day aging period, it drops from 21 minutes to 11 minutes. Such a change would have a large effect on the prepreg processing, since gelation could occur before the prepreg layers have been properly consolidated and excess resin has been squeezed out. Of the physical properties, the gel time is by far the most sensitive to the aging. However, it should not be considered sufficient as a control method because it may not be sensitive to all the variations in composition which can occur.

The mechanical testing results are given in Figure 15. The substantial degree of scatter observed makes it difficult to discern any correlation between mechanical properties and prepreg aging time. If there is an effect, it is not particularly strong. *However, this does not mean that the prepreg aging is insignificant in terms of its effect on the mechanical properties*. It must be remembered that these results were obtained for "ideal" specimens, simple flat panels made under laboratory conditions. For larger, more complex parts made in a factory environment, the effects would almost certainly be much more important, although to confirm this would require an expensive test program involving the sacrifice of real parts made from aged prepreg. Figure 14 shows that when the prepreg is exposed for 66 days, the gel time drops from 21 to 7 minutes, yet there is no significant effect on the resin flow value. This is because under the test conditions used, the resin flow occurs quickly and is complete before the resin gels, even for the aged prepreg. The same applies to the laboratory test panels. For a larger part, however, the path followed by the volatile materials and the excess resin as they leave the part is longer and more complex, so a longer time is required. A lower gel time would mean that the resin could gel before all volatile materials are removed and before excess resin has had time to flow out of the system. The higher porosity and lower fibre/resin ratio would lead to poorer mechanical properties. In addition, the long-term behaviour could be affected to a greater extent than the short-term properties, which are free from the effects of environmental exposure. Thus, the results given here should not be interpreted as showing that the aging has no effect on the mechanical properties. *Instead, they show that the standard laboratory mechanical tests using small panels are not capable of detecting significant chemical changes which are almost certain to affect the manufacture of more complex parts.* However, these changes are easily detected using physicochemical methods such as FT-IR, liquid chromatography, and thermal analysis.

A sheet of prepreg exposed for 50 days at 22°C but in a dry atmosphere was found to undergo aging at a slower rate than in the humid atmosphere. The changes observed corresponded to about 35 days aging at 50% R.H. On the other hand, a sample kept in a freezer for 87 days at -25°C showed no detectable change, showing that freezer storage effectively prevents chemical aging.

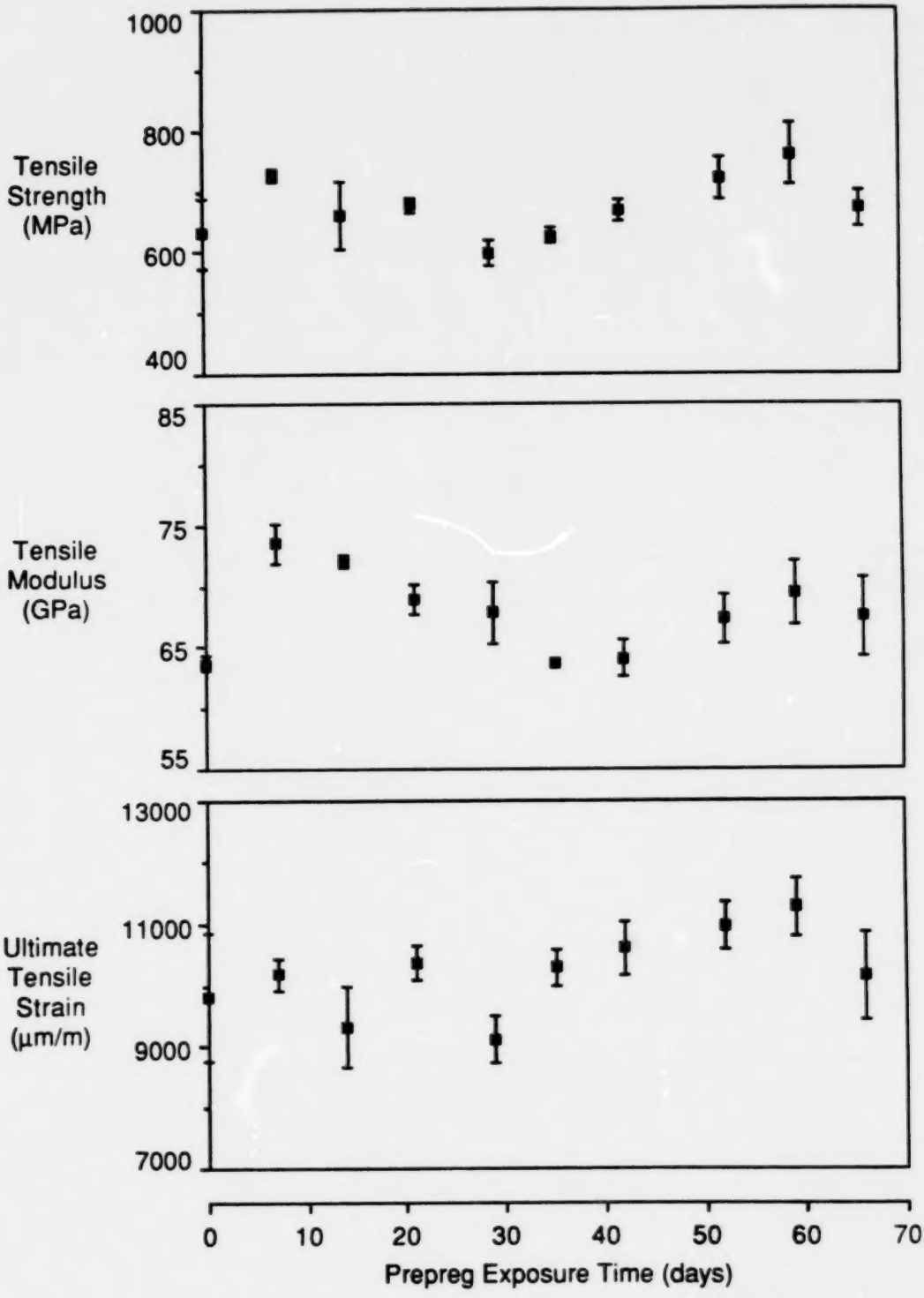


Figure 15 (a). Results of mechanical testing (tensile properties) of panels made from aged Narmco 5208/WC3000 prepreg.

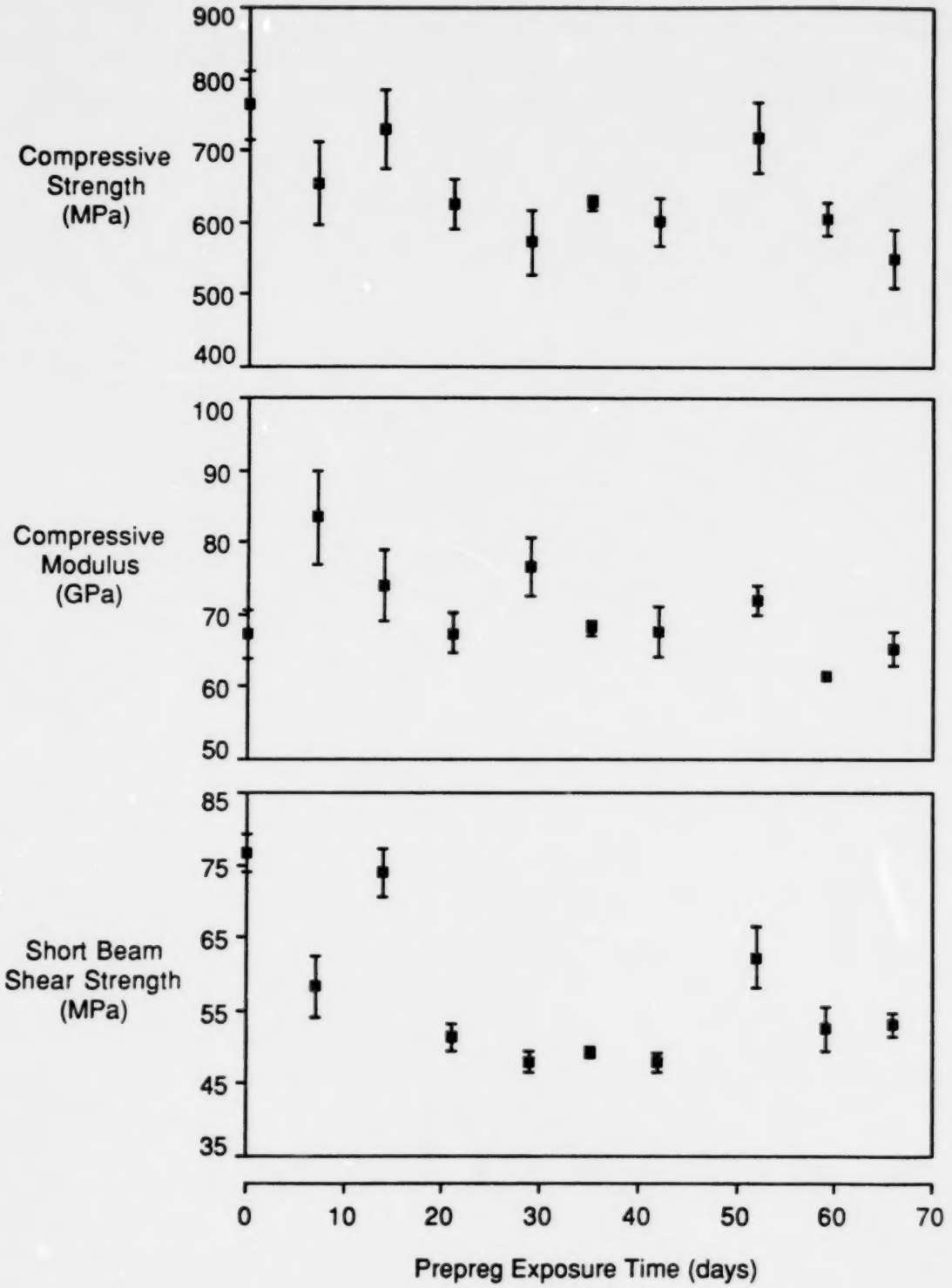


Figure 15 (b). Results of mechanical testing (compressive and short beam shear properties) of panels made from aged Narmco 5208/WC3000 prepreg.

4. APPLICATION TO OTHER SYSTEMS

Although the methods described in Chapter 2 were developed using Narmco 5208, they may also be applied to other commercial systems to obtain both qualitative and quantitative information. Depending on the system, they may need to be modified in order to give optimum results. This chapter describes some results obtained when these methods were applied without modification to a few other commonly used systems. It must be emphasized that time did not permit to do a complete analysis, nor to perform any further optimization of the methods. However, it is felt that these "preliminary" results, together with a few comments, will demonstrate the general applicability of these methods and may be of help to someone interested in extending them to other commercial products.

The RPLC chromatograms presented in this section were all obtained using a Hypersil MOS-1 column without the addition of acetophenone as an internal standard.

4.1 FIBERITE 976

Like Narmco 5208, this is an epoxy system cured at 350°F (177°C). The prepreg sample examined consisted of unidirectional tape based on T300 carbon fibres. Figure 16 shows the infrared transmission spectra of a thin film of extracted resin (cast from acetone) before and after curing (3 hours at 350°F). They are very similar to those of Narmco 5208 (Figure 2). However, a closer comparison of the spectra, together with those of Araldite MY 720, Hardener HT 976, and Epi-Rez SU-8 (shown in Figure 17), shows up certain differences, which are best seen by performing spectral subtractions. To summarize the results, Fiberite 976 does not appear to contain any bisphenol A Novolac epoxy (SU-8) and the content of DDS (HT 976) appears to be somewhat higher than in Narmco 5208.

Figures 18 and 19 give the IR spectra obtained directly from prepreg by attenuated total reflection (45° Ge prism) and by diffuse reflection. These are good-quality spectra which could be used for the same purposes as in the case of Narmco 5208.

Figure 20 shows the RPLC chromatogram. The most prominent features are the DDS peak (showing some splitting) around 3.5 min and the TGDDM peak at 8.3 min. Comparison with the chromatogram of Narmco 5208 in Figure 7 shows up the conspicuous absence of the peaks characteristic of bisphenol A Novolac epoxy (DGEBA monomer near 10 min, higher oligomers between 15 and 20 min). The TGDDM-DDS reaction product peak at 7.2 min is also relatively weak compared to Narmco 5208, suggesting a lower degree of advancement. There are no strong peaks near 5.1 min which might interfere with acetophenone if it were added as an internal standard.

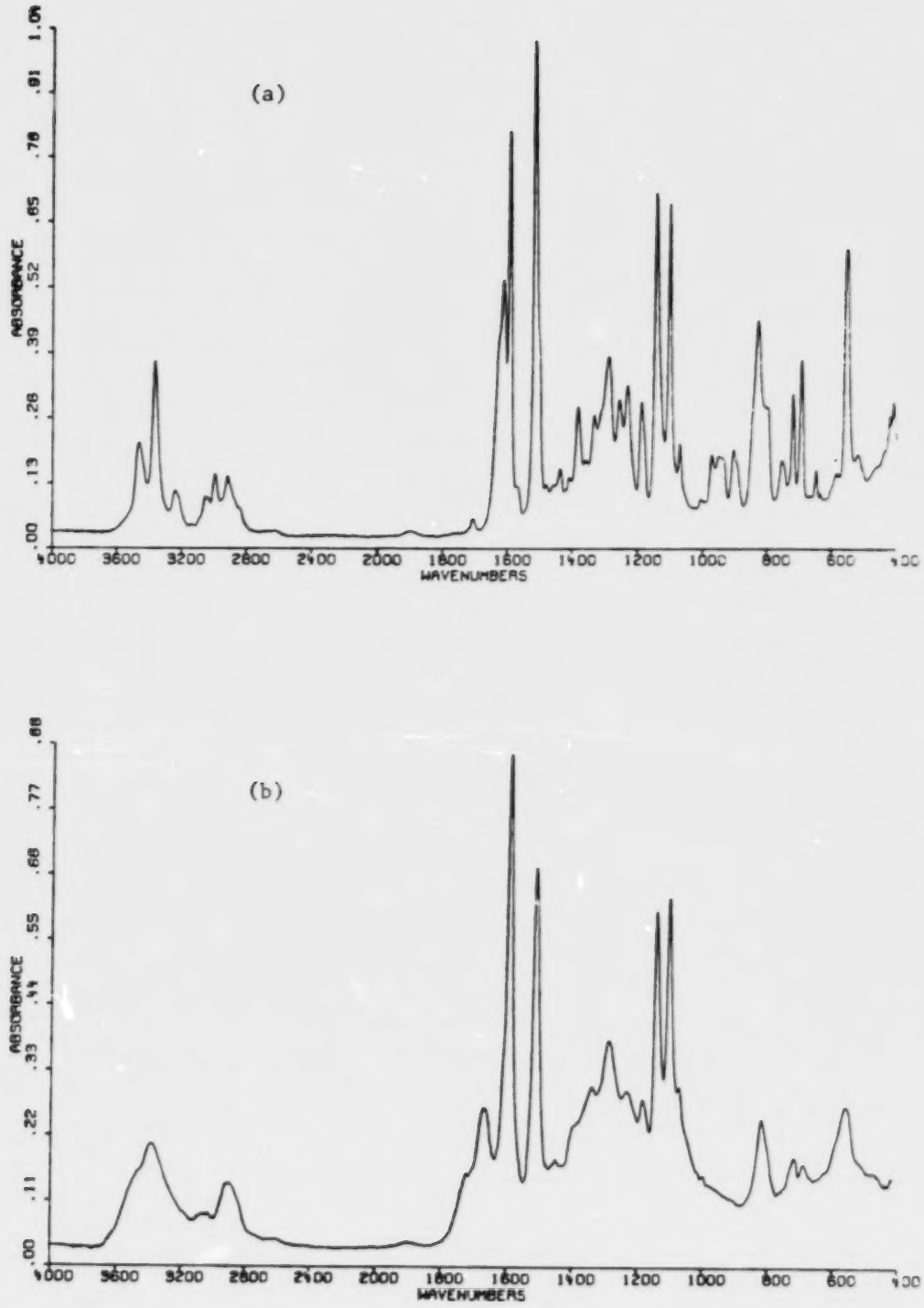


Figure 16. FT-IR transmission spectra of a thin film of Fiberite 976 resin: (a) uncured (b) cured.

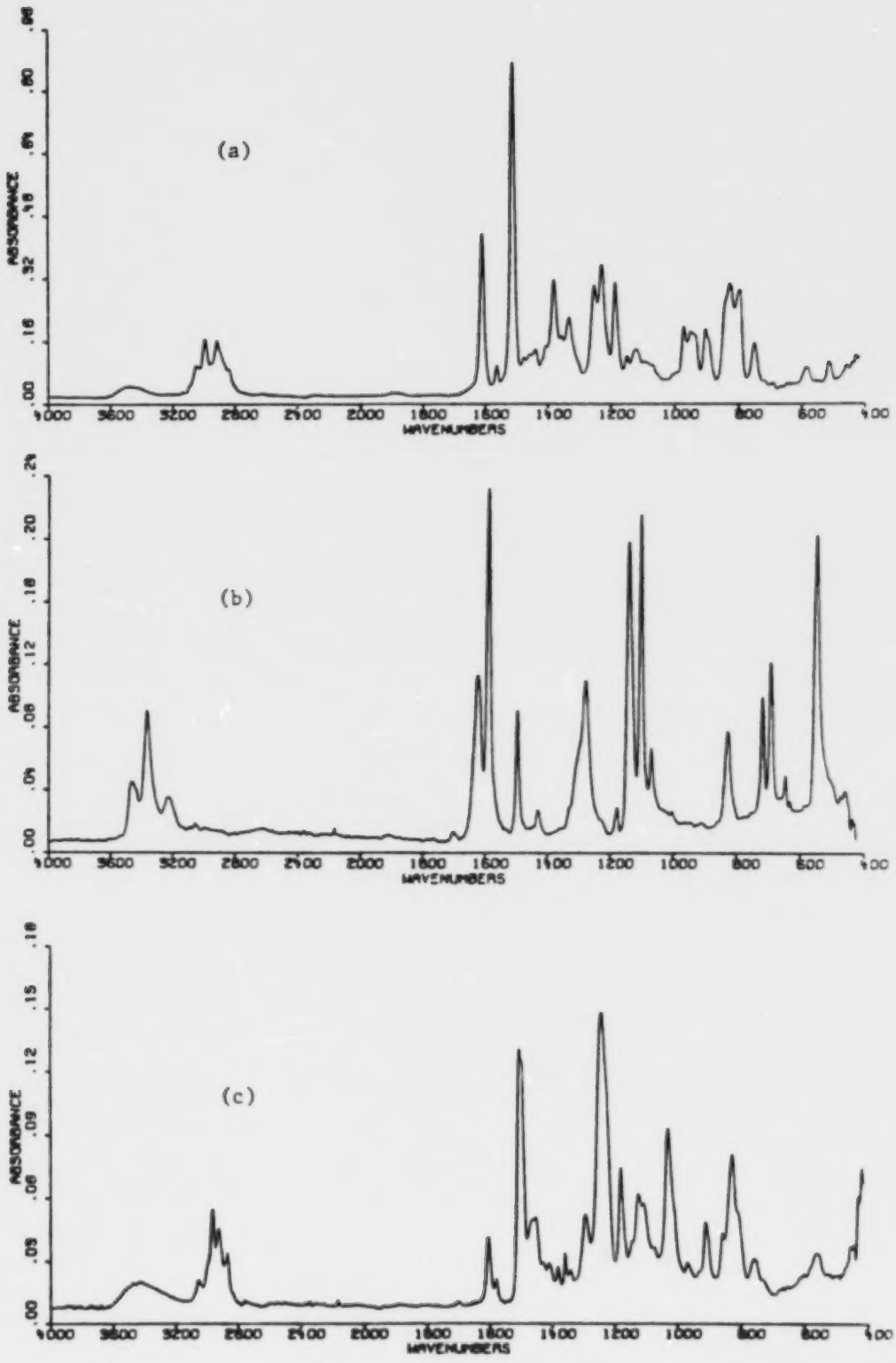


Figure 17. FT-IR transmission spectra of thin films of (a) Ciba-Geigy Araldite MY 720, (b) Ciba-Geigy Hardener HT 976, and (c) Celanese Epi-Rez SU-8.

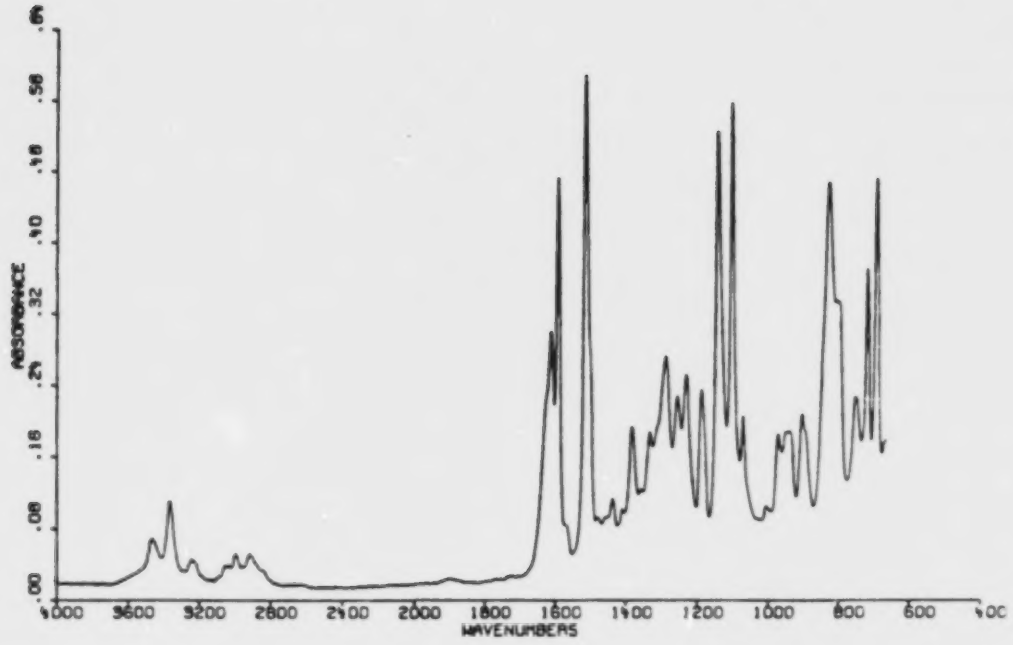


Figure 18. FT-IR attenuated total reflection spectrum of Fiberite 976 carbon-fibre prepreg.

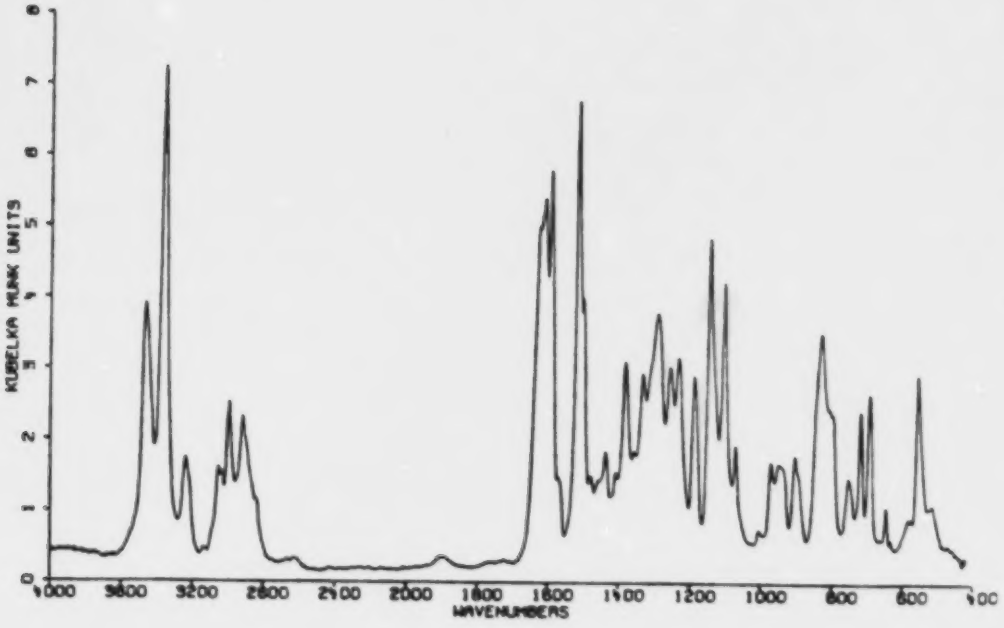


Figure 19. FT-IR diffuse reflection spectrum of Fiberite 976 carbon-fibre prepreg.

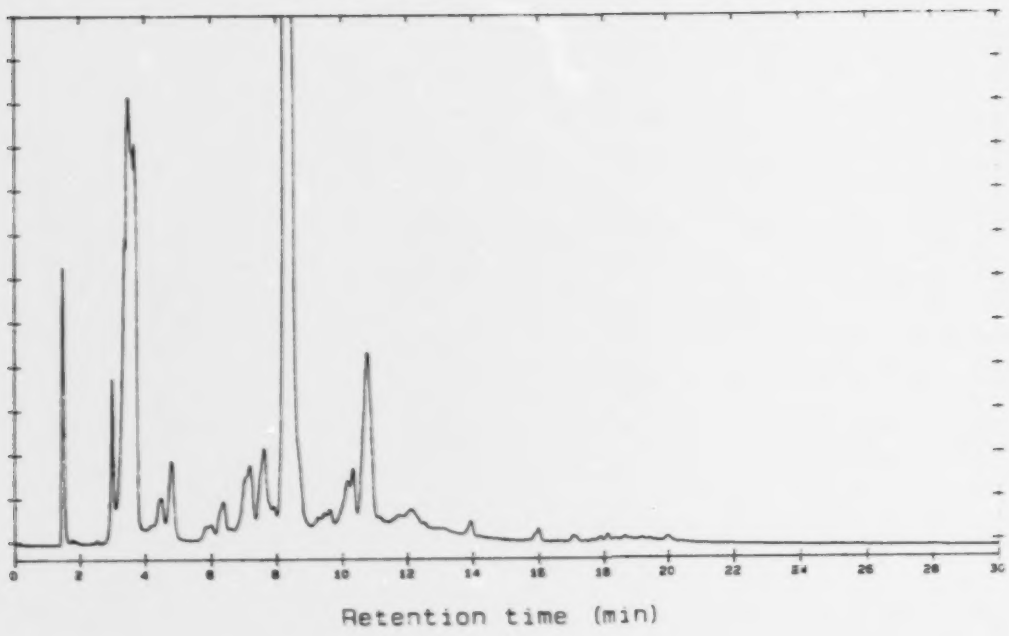


Figure 20. RPLC chromatogram of Fiberite 976 resin.

In summary, the major components of Fiberite 976 appear to be DDS and a TGDDM-type epoxy resin. The analytical methods developed for Narmco 5208 should be very easily applicable.

4.2 FERROPREG CE-9000-2

This is also an epoxy system cured at 350°F. Unlike all the cases previously discussed, which involved carbon fibre reinforcement, the samples examined here were reinforced with either Kevlar® (plain weave fabric) or glass (unidirectional) fibres.

Figure 21a shows the transmission IR spectrum of a thin film of resin obtained by acetone extraction of the Kevlar prepreg. From the peaks at 3600-3200, 1293, 1145, 1105, 721, 695, and 553 cm^{-1}, the hardener is readily identified as DDS. The epoxy is not TGDDM, however. The shape of the C-H peaks (3100-2800 cm^{-1}) and the positions of the remaining ones (1595, 1510, 1454, 1242, 1035, 972, 914, 831, 758 cm^{-1}) suggest that the main epoxy resin is of the phenol Novolac type, for example the Dow DEN or Ciba-Geigy EPN series of products [17]. Figure 21b gives the spectrum of the same film after curing for 2.5 hours at 350°F. The weak peak observed at 1707 cm^{-1} in Figure 21a disappears on curing, so it is probably due to residual acetone from the extraction. The epoxide peak at 914 cm^{-1} also disappears on curing, and it should be possible to monitor the epoxide content by taking the ratio of this peak with respect to the aromatic ring peak at 1510 cm^{-1}. Similarly, as for Narmco 5208, the sulphone peaks at 1145 and 1105 cm^{-1} could be used to check the DDS content.

When reflection techniques are used to measure the spectrum directly from prepreg, the effect of the reinforcement must be considered. Carbon fibres give rise to a broad "background" absorption without distinctive peaks [2], so the resin peaks are clearly seen. Kevlar, on the other hand, being an aromatic polyamide, has distinct peaks of its own, as shown in the diffuse reflection spectrum of woven Kevlar cloth in Figure 22. These could interfere with the peaks of the resin in the prepreg spectrum.

Figure 23 shows the prepreg spectrum obtained by ATR with a 45° Ge prism. Except for the solvent peak at 1707 cm^{-1} it is very similar to the transmission spectrum of the resin, and there is no sign of any Kevlar absorption. This is because on the surface of the prepreg there is a thin layer of resin, and the infrared beam does not penetrate deep enough to "see" the Kevlar fibres. Even with a KRS-5 prism, which results in a higher penetration depth, there is no evidence of Kevlar absorption. However, some peaks are distorted because of refractive index effects [2]. Thus, when ATR is used to measure prepreg, the nature of the reinforcement seems to be of little importance.

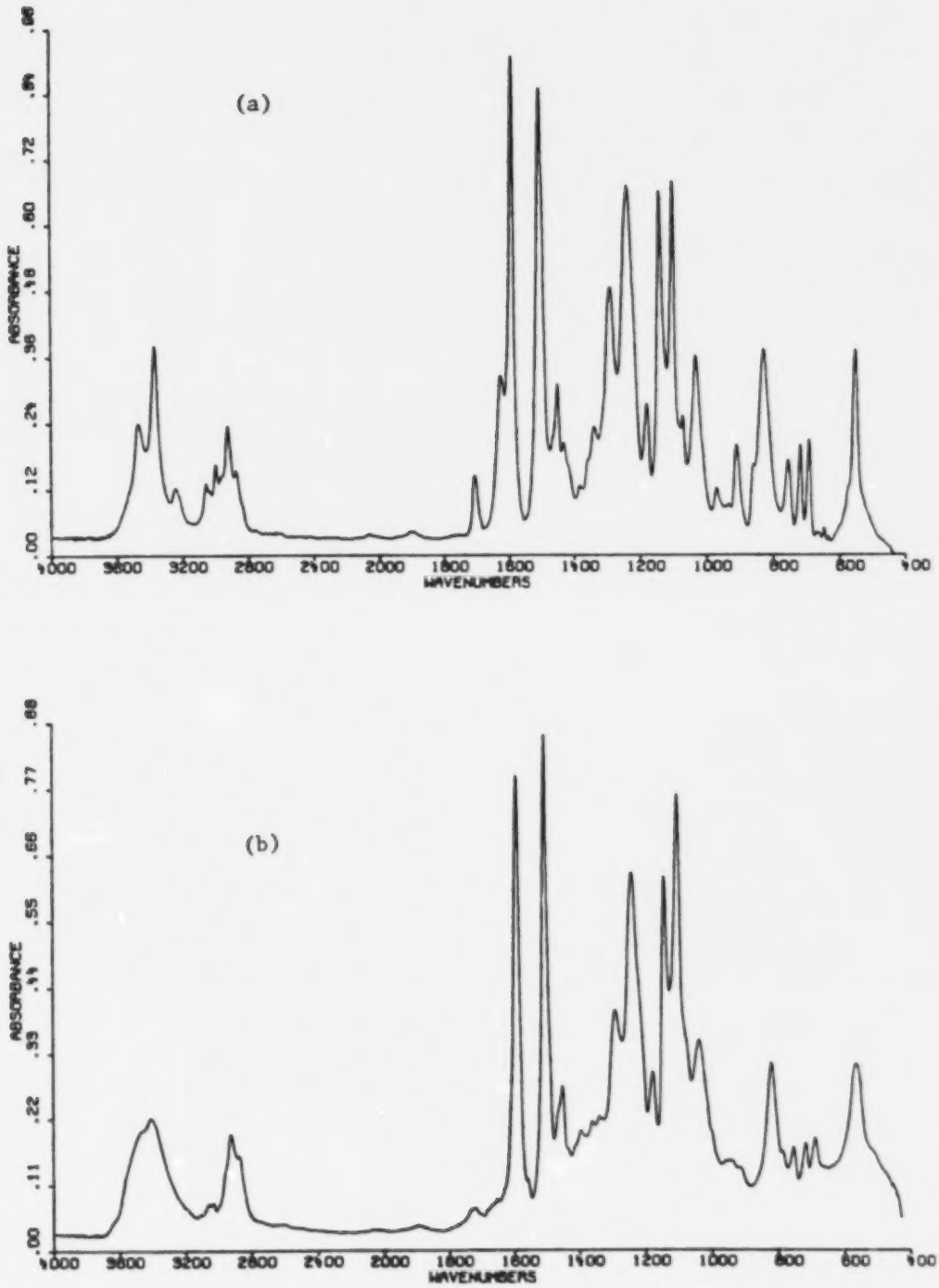


Figure 21. FT-IR transmission spectra of a thin film of Ferropreg CE-9000-2 resin: (a) uncured (b) cured.

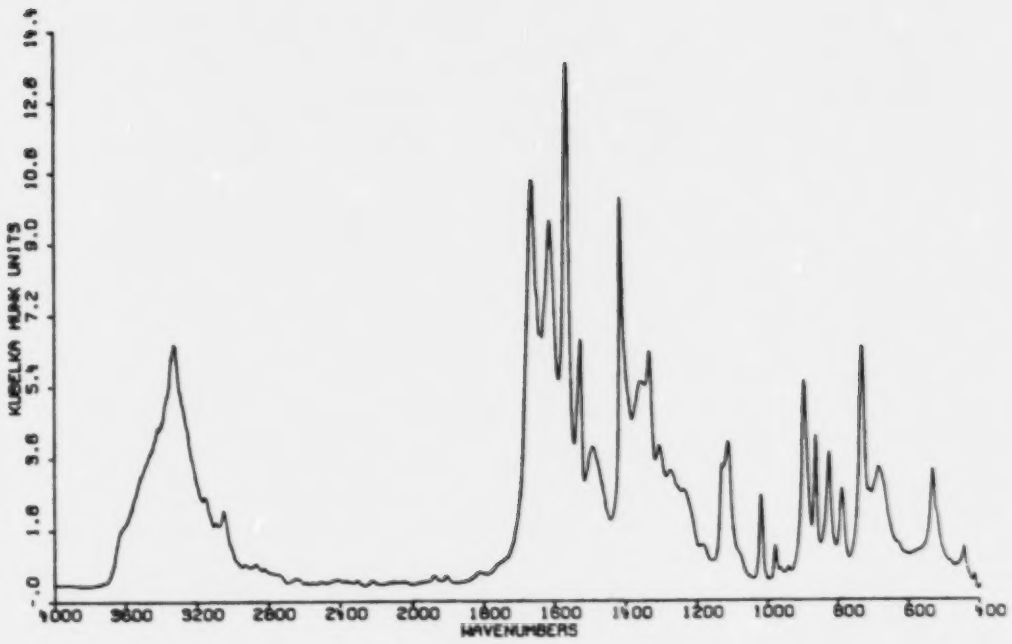


Figure 22. FT-IR diffuse reflection spectrum of plain-weave Kevlar cloth.

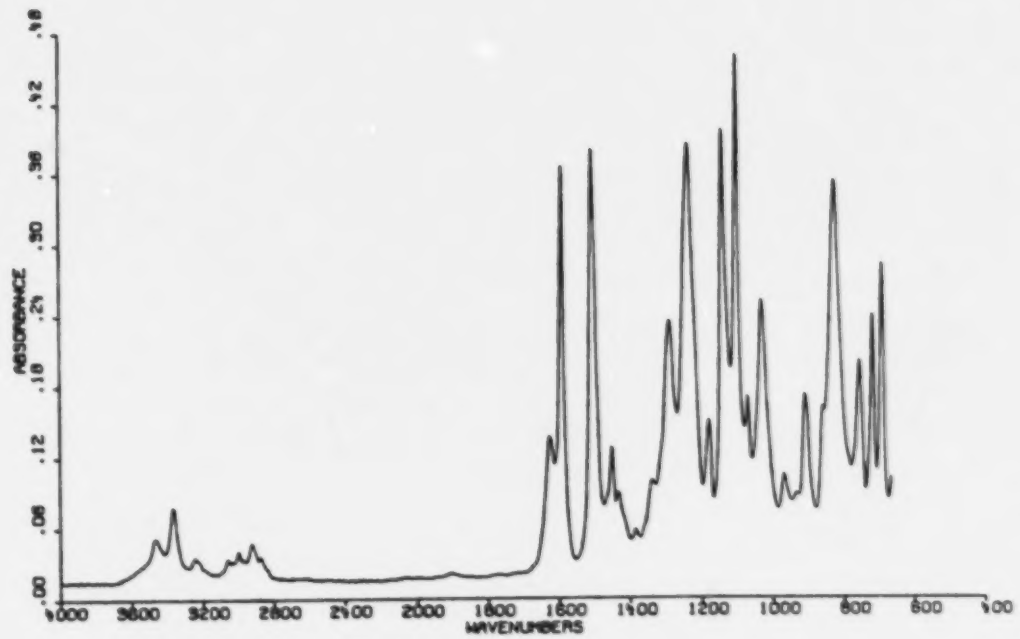


Figure 23. FT-IR attenuated total reflection spectrum of Ferropreg CE-9000-2 Kevlar prepreg.

This is not the case for diffuse reflection. Figure 24 gives the DR spectrum as recorded for the Kevlar prepreg. In DR, the penetration depth is much higher and the beam penetrates to the Kevlar fibres. Because the Kevlar and the resin have similar refractive indices, there is very little reflection at the fibre-resin interface, so the beam is not back-reflected out of the sample. Consequently, the IR detector sees mainly the Fresnel reflection from the front surface of the prepreg. The overall reflectance is quite low, and although peaks are observed, they are highly distorted because of refractive index effects. This greatly limits the amount of information available from the DR spectrum, and it is useless to perform the Kubelka-Munk transformation since it does not apply. This is not so in the case of carbon fibres, whose refractive index appears to be sufficiently different from that of the epoxy matrix to provide a high degree of back-scattering and give good spectra, such as Figure 5. Unfortunately, glass fibres behave only slightly better than Kevlar, as shown by Figure 25.

RPLC gives the chromatogram shown in Figure 26. Again, the DDS peak near 3.5 min shows splitting. The remaining peaks have not been identified. The ones near 4.6 min could cause problems if acetophenone were used as internal standard; an alternative might have to be found. It is unlikely that the peak at 8.2 min is due to TGDDM; instead it and its companion at 8.7 min probably arise from the epoxy phenol Novolac. The peak at 9.8 min could indicate the presence of a DGEBA-containing epoxy resin as well.

The HPSEC chromatogram (Figure 27) shows a distinct DDS peak around 6.9 min but no TGDDM peak at 7.2 min. The main epoxy peak occurs at 6.3 min, and there are also some higher-molecular-weight components which appear between 4.6 and 6 min.

The pyrolysis gas chromatogram is shown in Figure 12b. Although quite different from that of Narmco 5208 (Figure 12a), it has some peaks in common, most notably phenol and aniline at 8.2 and 8.9 min respectively. The aniline peak is related to the presence of the aromatic amine hardener DDS.

The combined results suggest that the main components of this system are an epoxy phenol Novolac and DDS. There may also be another epoxy resin based on DGEBA.

4.3 FERROPREG CE-306

This is an epoxy-based system with a recommended cure temperature of 260°F (126°C). The prepreg sample studied was reinforced with plain-weave Kevlar cloth. When acetone extraction was performed to cast a film for IR spectroscopy, the resulting solution was cloudy. The spectrum showed that the hardener is dicyandiamide, also known as cyanoguanidine or DICY:

Figure 24. FT-IR diffuse reflection spectrum of Ferropreg CE-9000-2 Kevlar prepreg.

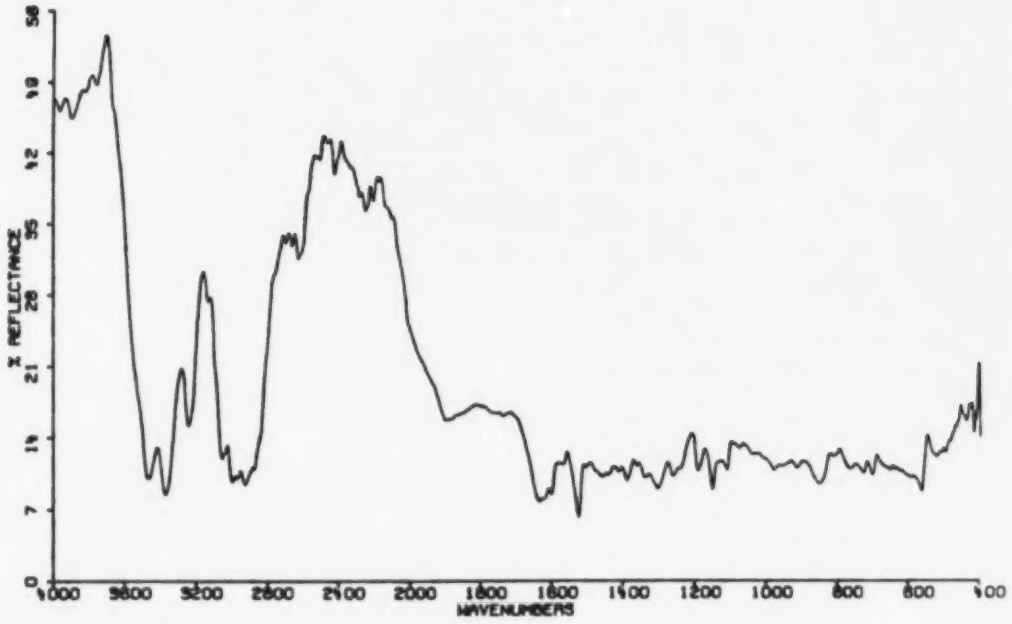


Figure 25. FT-IR diffuse reflection spectrum of Ferropreg CE-9000-2 glass-fibre prepreg.

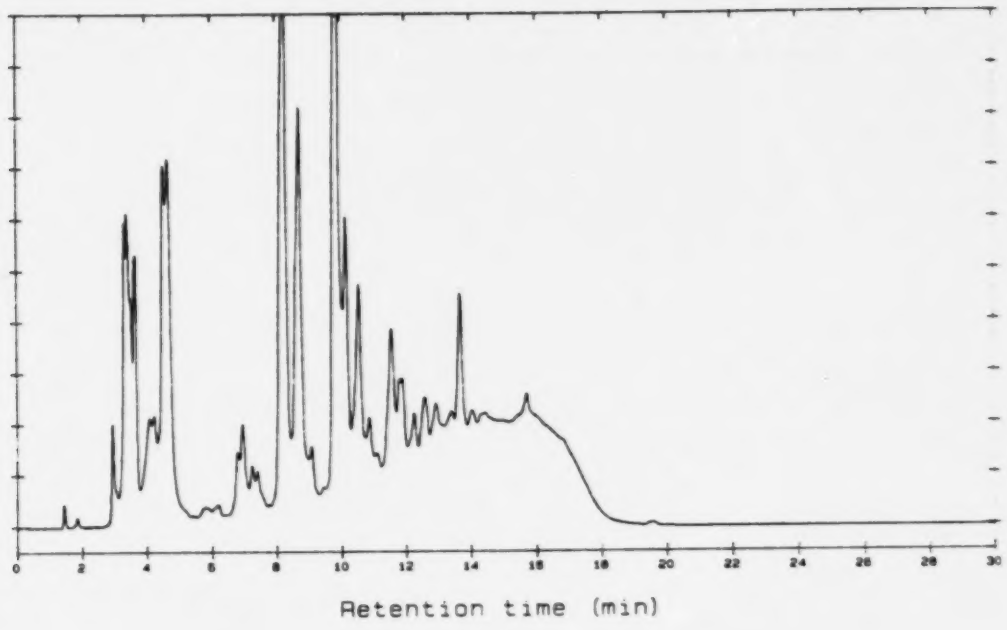


Figure 26. RPLC chromatogram of Ferropreg CE-9000-2 resin.

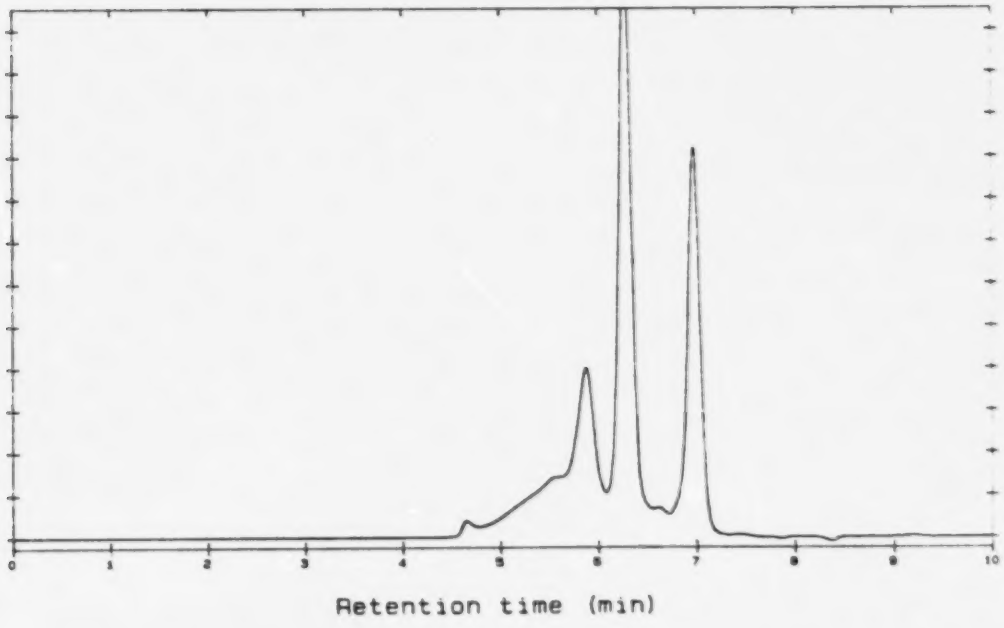


Figure 27. HPSEC chromatogram of Ferropreg CE-9000-2 resin.

This is a very polar compound with limited solubility in many organic solvents, including epoxy resins [18]. When used as a curing agent, it is generally present in the form of fine particles dispersed in the resin. In many such cases, if acetone is used as a solvent for resin extraction, a cloudy solution is obtained from which it is difficult to prepare uniform films because of their non-homogeneous nature. It was found that spectra of films prepared in this way were not very reproducible. It has been reported [19] that a 50:50 mixture of tetrahydrofuran and dimethylformamide is a better solvent and gives films of better quality. When this mixture was used, the solution was only very slightly cloudy. Films were prepared by evaporating the solvent, using a vacuum to remove the last traces. The resulting spectrum is given in Figure 28a. The two distinct peaks at 2165 and 2208 cm^{-1} are due to the cyano groups of the DICY, and have been attributed respectively to the two forms shown above [20]. Other distinct peaks arising from the DICY, whose spectrum is shown in Figure 29a, are located at 3600-3100, ≈1650, 929, and 668 cm^{-1}. The remaining peaks are due mainly to the epoxy resin, which appears to be of the standard bisphenol A (non-Novolac) type, such as Araldite 6010 (Figure 29b), Dow DER 331, or Shell Epon 828 [17]. Figure 28b shows the spectrum of a film of Ferropreg CE-306 after curing for 3 hours at 130°C. The N-H bands of the DICY at 3600-3100 cm^{-1} have been replaced by an O-H band, and the peaks near 2200 cm^{-1} have disappeared. Also, the epoxide ring peak at 915 cm^{-1} has disappeared on reaction of the epoxide groups. In principle, the IR spectrum can be used for quantitative analysis, but the situation is somewhat more complicated than for Narmco 5208. First of all, there is the difficulty of preparing uniform films because of the limited solubility. Secondly, the epoxide band at 915 cm^{-1} coincides with the small DICY peak at 929 cm^{-1}. Thirdly, the DICY peaks near 2200 cm^{-1}, which could be used as an indicator of the DICY content, are affected by the curing of the resin. Consequently, before IR could be used for quantitative purposes, the importance of each of these factors would have to be investigated.

When ATR is used to measure the spectrum, an interesting phenomenon is observed. Figure 30 gives the spectrum obtained with a 45° Ge prism. Comparison with the transmission spectrum of Figure 28a shows that the DICY peaks are practically nonexistent in the ATR spectrum. The probable reason is the heterogeneity of the resin system. In ATR, only the first few micrometres of the surface layer are "seen", and this appears to consist mainly of epoxy resin; the DICY particles dispersed in the resin are located at a

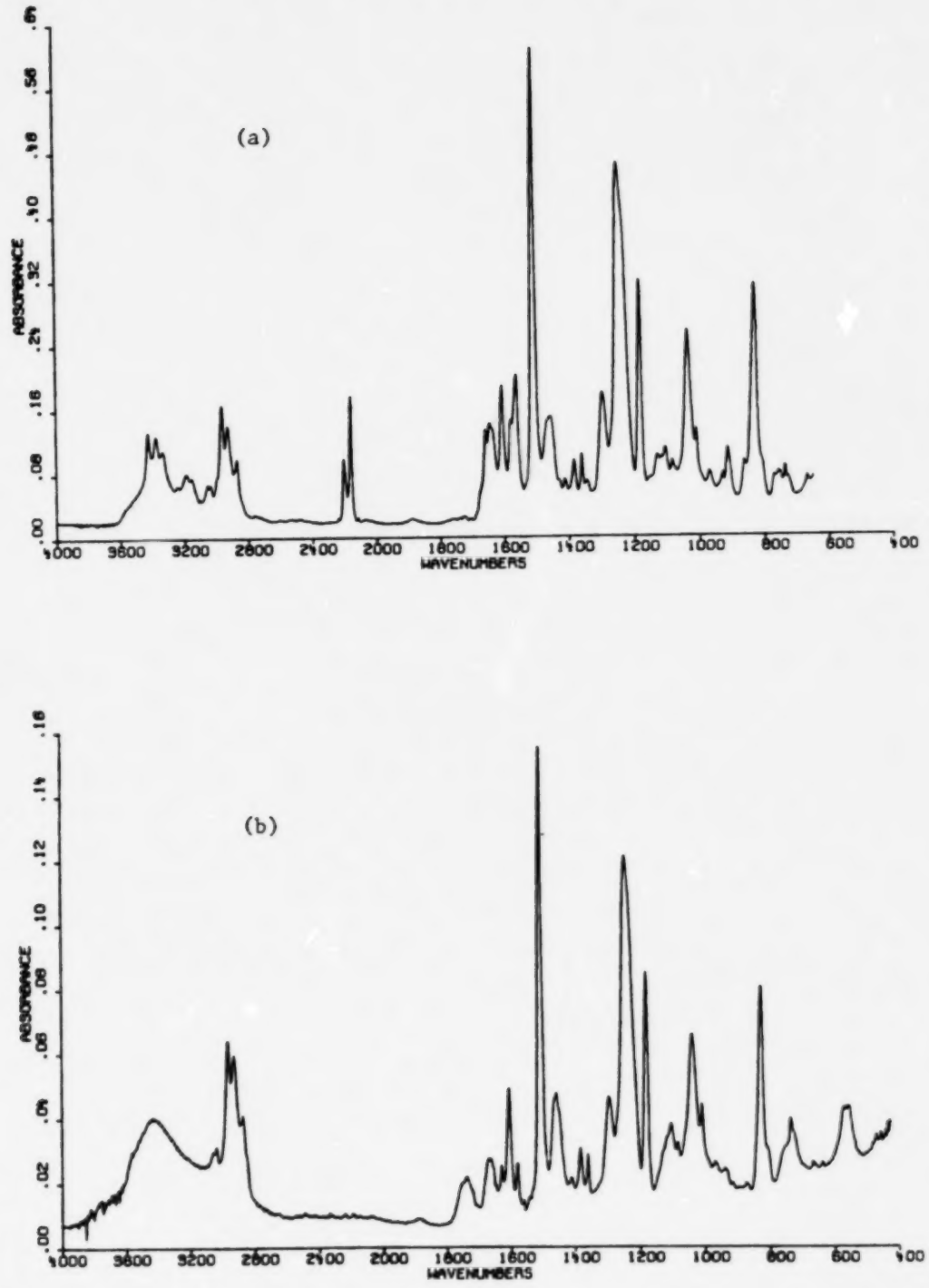


Figure 28. FT-IR transmission spectra of a thin film of Ferropreg CE-306 resin: (a) uncured (b) cured.

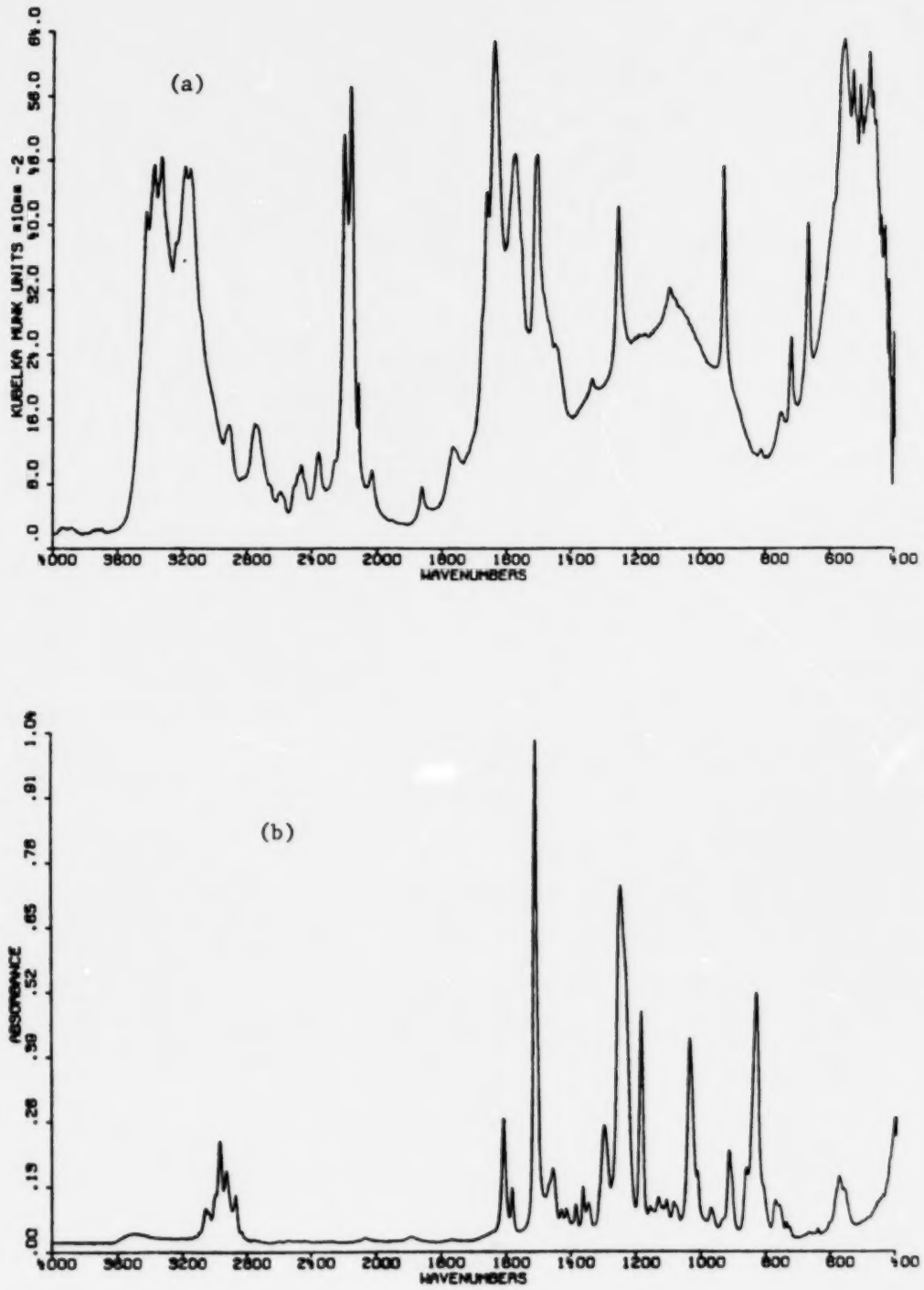


Figure 29. FT-IR transmission spectra of thin films of (a) DICY and (b) Araldite 6010.

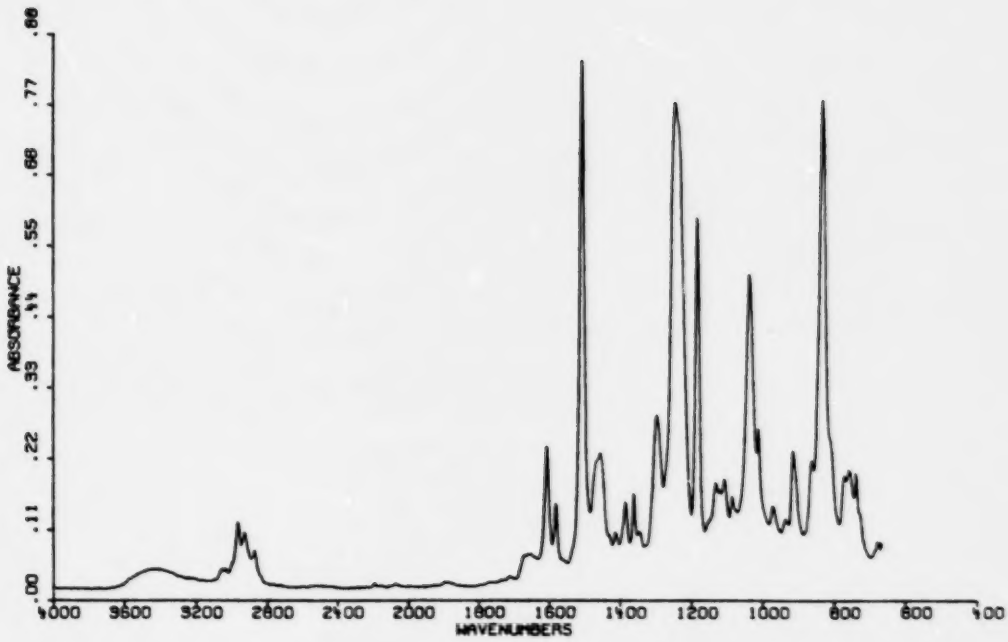


Figure 30. FT-IR attenuated total reflection spectrum of Ferropreg CE-306 Kevlar prepreg.

greater depth. Spectra were also recorded using a KRS-5 prism (greater penetration depth) but the DICY peaks were only slightly more evident and nowhere near the intensity observed in transmission. Thus ATR is not suitable for heterogeneous systems such as those containing DICY.

Figure 31 shows diffuse reflection spectra of both prepreg and a cured panel. The same problem is encountered as in the case of Ferropreg CE-9000-2. Because the reinforcement is Kevlar, only front-surface reflection is observed and the spectra provide rather limited information. Nevertheless, the DR spectrum can serve to identify the system. This is facilitated by taking appropriate derivatives of the spectra. Figure 32 compares the first derivative of the DR spectrum with the second derivative of the transmission spectrum of a thin film of cured resin. In spite of the high noise level, it can be seen that the two traces are quite similar and show distinct peaks at much the same frequencies. These peaks, which arise from the epoxy resin, can provide useful information as to the composition of the system.

As expected, the RPLC chromatogram (Figure 33) is quite different from the previous ones. There are several significant peaks, of which the easiest to assign are DICY at 2.5 min and DGEBA at 10.0 min. Others occur at 5.8, 13.9, 16.0, 18.1, and 19.2 min. The one at 5.8 min would probably interfere with acetophenone internal standard.

In the HPSEC chromatogram (Figure 34), a number of peaks are observed. The one with the longest retention time, near 6.9 min, is also the strongest. It probably corresponds to the DICY. The next strongest is at 6.7 min and five others occur between 4.5 and 6.3 min.

Like the RPLC chromatogram, the pyrolysis gas chromatogram (Figure 35b) is also quite different from those of Narmco 5208 and Ferropreg CE-9000-2 (Figure 12). Three strong peaks stand out, and the one at 8.4 min probably corresponds to phenol, as in the case of Narmco 5208. The absence of a strong aniline peak at 8.9 min is no doubt related to the lack of DDS hardener in this system.

To summarize, the main components of Ferropreg CE-306 appear to be a standard bisphenol A type epoxy resin with DICY as hardener.

4.4 NARMCO 3203

This is an epoxy-based system with a cure temperature range of 250 – 300°F (121 – 149°C). The sample studied was reinforced with woven carbon fibre cloth similar to that in the Narmco 5208 system.

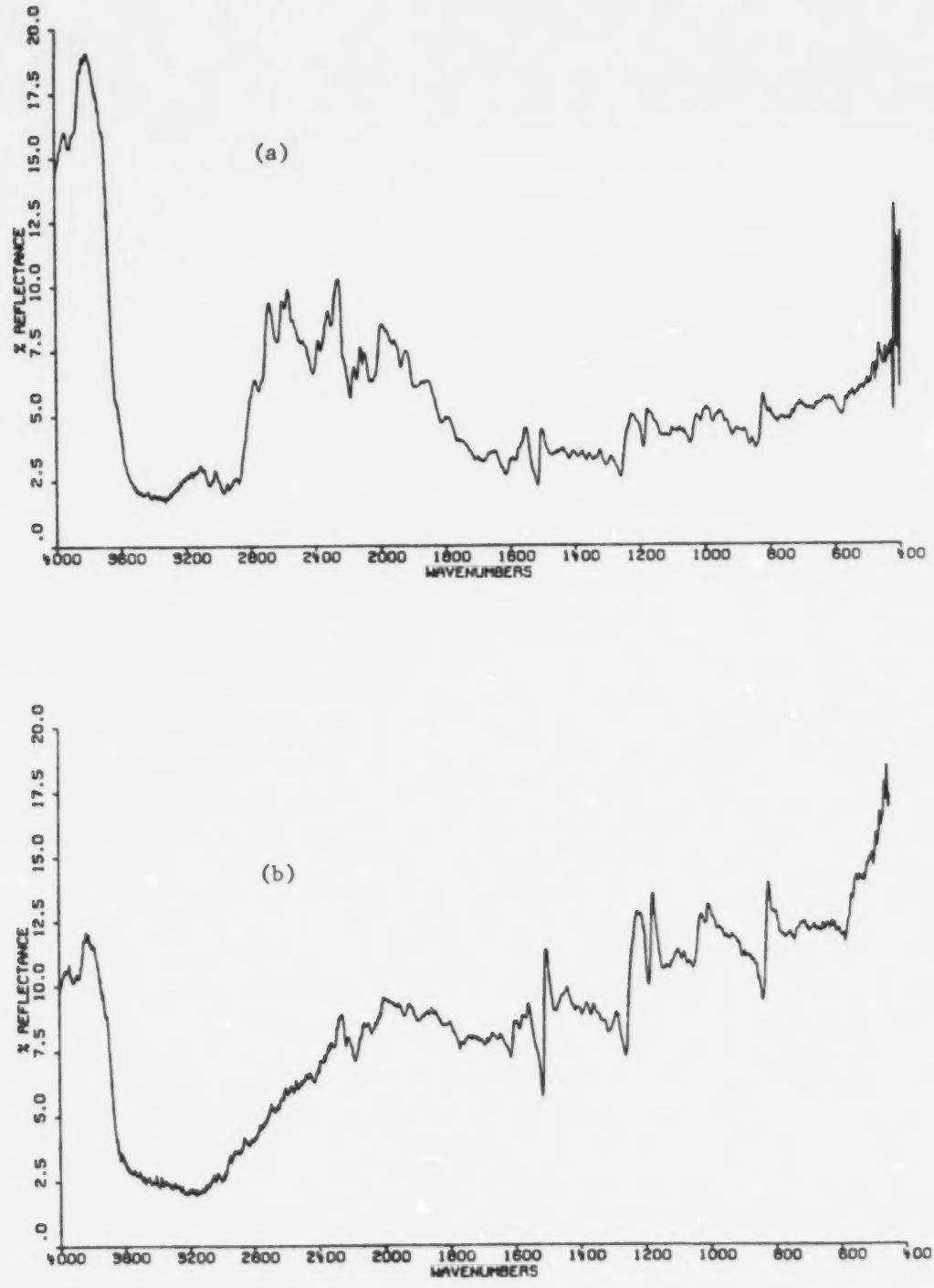


Figure 31. FT-IR diffuse reflection spectrum of (a) Ferropreg CE-306 Kevlar prepreg and (b) cured panel.

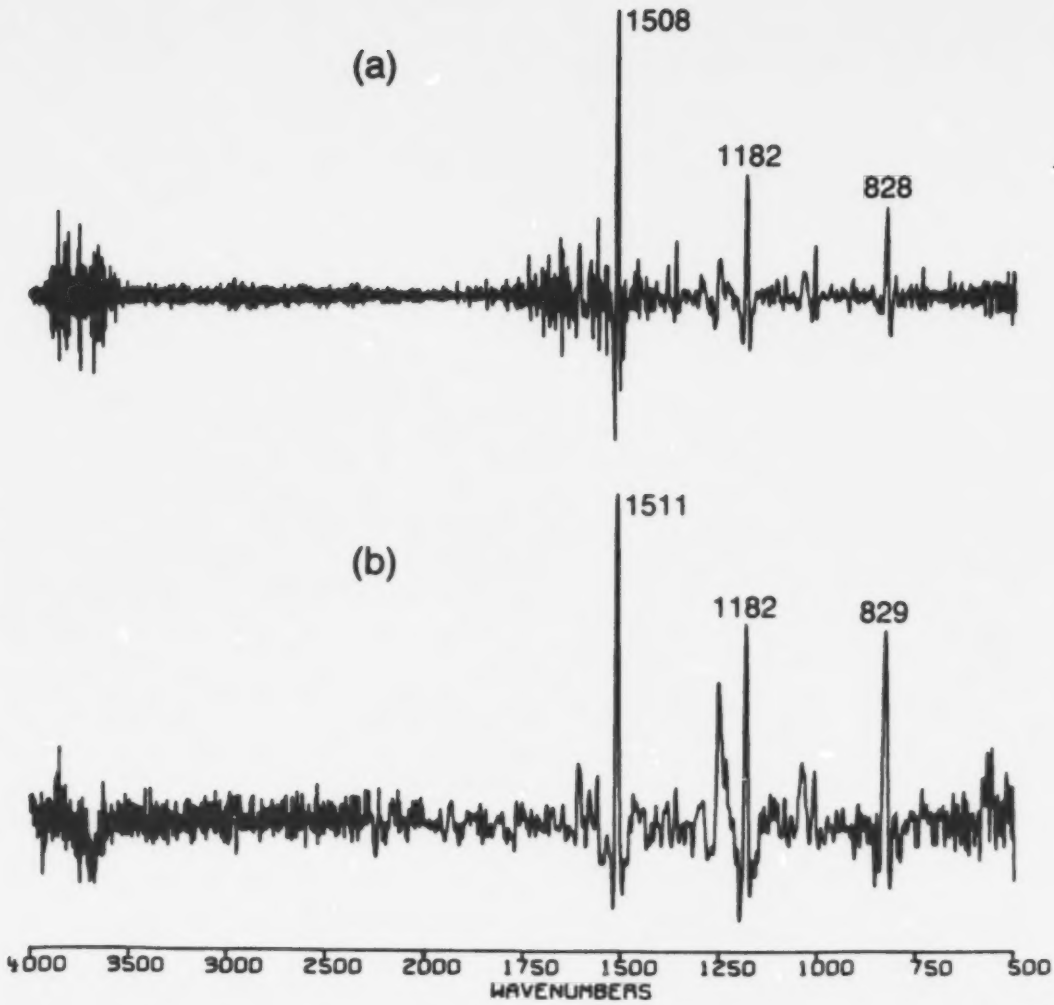


Figure 32. Derivative traces of Ferropreg CE-306 spectra: (a) second derivative of transmission spectrum of film of cured resin; (b) first derivative of diffuse reflection spectrum of Kevlar-reinforced cured panel.

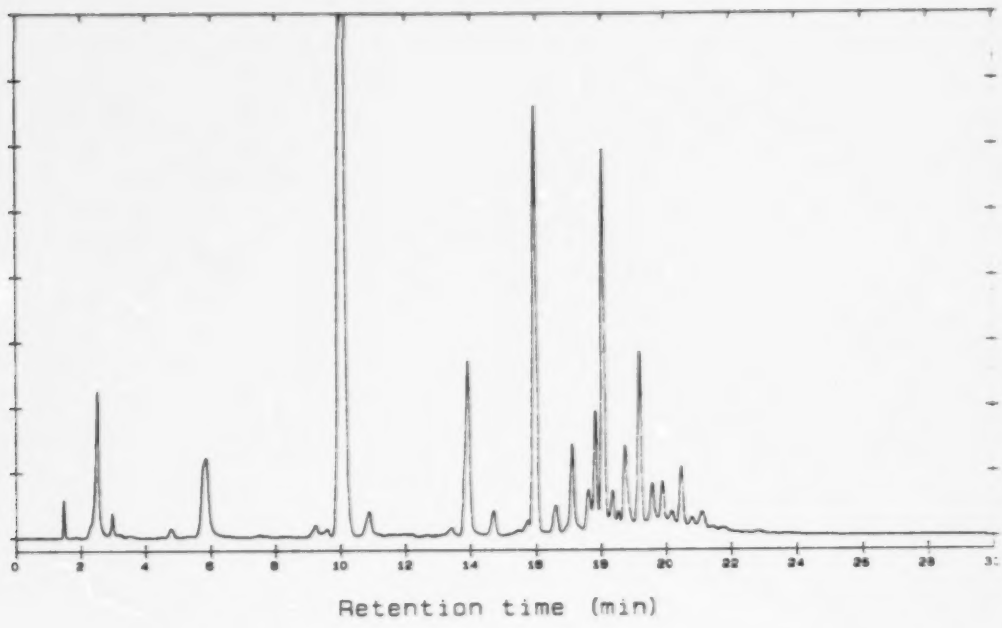


Figure 33. RPLC chromatogram of Ferropreg CE-306 resin.

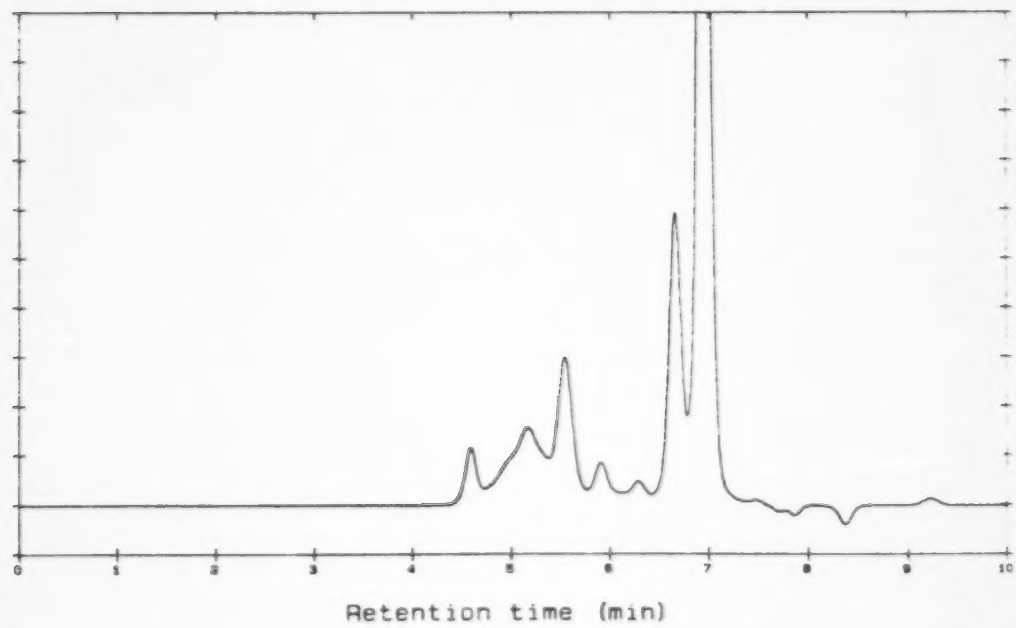


Figure 34. HPSEC chromatogram of Ferropreg CE-306 resin.

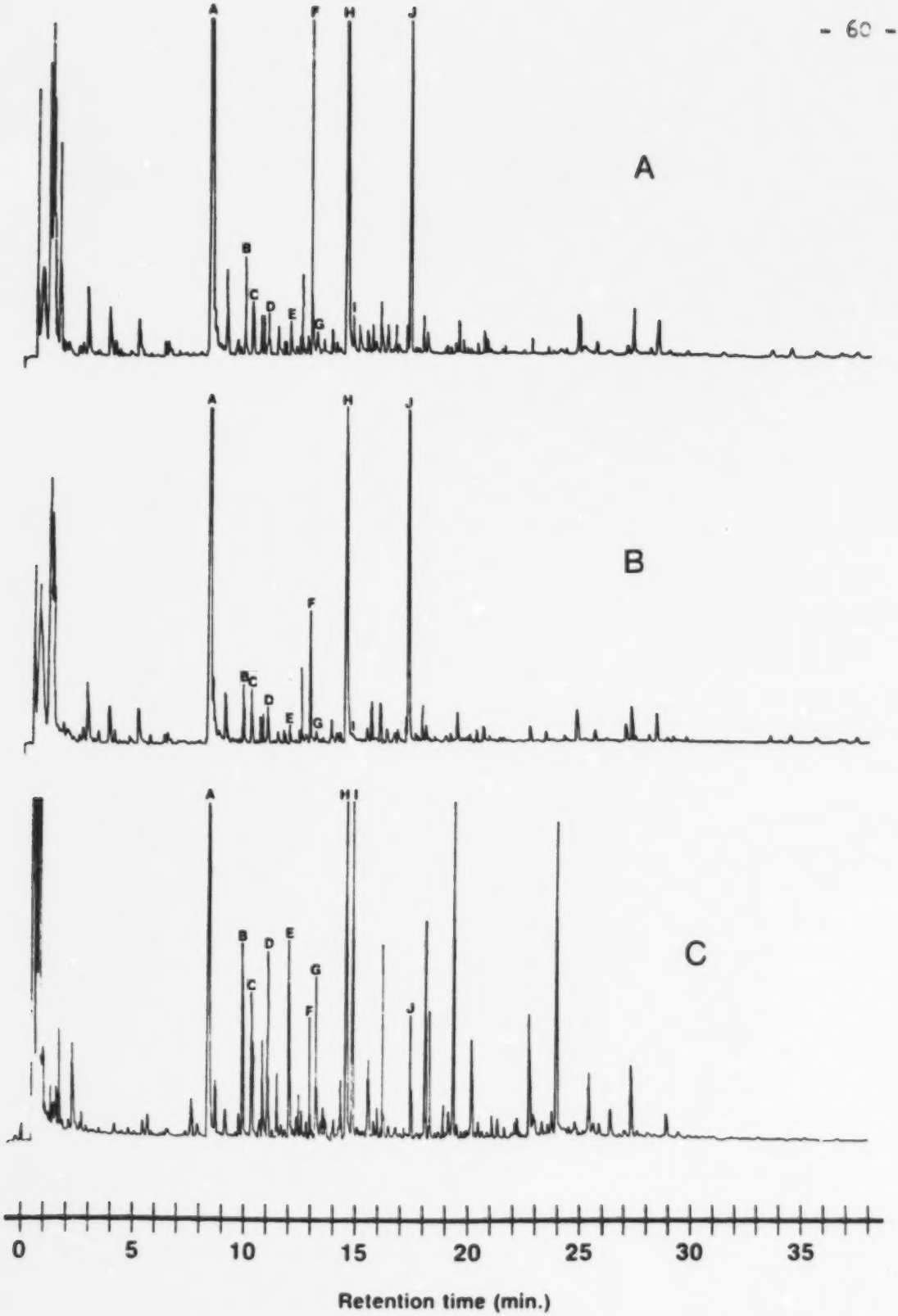


Figure 35. Py-GC chromatograms of (a) Narmco 3203/WC3000 prepreg, (b) Ferropreg CE-306 Kevlar prepreg, and (c) Araldite 6010 epoxy resin.

In terms of resin chemistry, this system was found to be similar to Ferropreg CE-306, so films for IR spectroscopy were prepared using a THF/DMF mixture. However, the extract was considerably more cloudy than in the Ferropreg case. The transmission spectra of uncured and cured resin are shown in Figure 36. They closely resemble those of Ferropreg CE-306. The ATR spectrum (Figure 37) is also similar to that of Ferropreg CE-306 and suffers from the same problem because of the heterogeneous nature of the matrix system. The DR spectrum (Figure 38) is better than that of the CE-306 because of the presence of carbon fibres rather than Kevlar. However, the DICY peaks are not as well defined as in the transmission spectrum.

Although the infrared spectrum of this system is quite similar to that of Ferropreg CE-306, this is not the case for the RPLC chromatogram (Figure 39). The DICY and DGEBA peaks at 2.5 and 10.1 min are similar, but the peak at 5.8 min is stronger. Also, the remaining strong peaks occur at different retention times (14.6, 17.9, 20.2, 20.6, and 21.6 min). In addition, there are two peaks of medium intensity at 8.4 and 8.9 min, similar to those seen in Ferropreg CE-9000-2 and attributed to epoxy phenol Novolac.

The HPSEC chromatogram (Figure 40) also shows significant differences compared to that of Ferropreg CE-306. The DICY peak at 6.9 min is still the strongest and the peak at 6.6 min is present, but the shape of the rest of the curve is different.

The Py-GC chromatogram, on the other hand, shown in Figure 35a, is very similar to that of Ferropreg CE-306.

The final conclusion, based on all the above results, is that Narmco 3203 and Ferropreg CE-306 are similar chemically but different in terms of molecular weight distribution. Liquid chromatography is much more sensitive to molecular weight variations than are infrared spectroscopy or pyrolysis – gas chromatography. The reason for the difference between the two systems could be that the epoxy resins used are of different molecular weight initially, or that one system is more polymerized than the other. If the latter is the case, Narmco 3203 would seem to be more polymerized, since it gives a more cloudy solution in THF/DMF. Also, the peak at 5.8 min in the RPLC chromatogram is stronger in the case of Narmco 3203. This peak could be due to a reaction product between DICY and epoxy. In any case, both systems appear to be based on a standard bisphenol A type epoxy with DICY as hardener, but the Narmco 3203 may also contain some epoxy phenol Novolac.

4.5 NARMCO RIGIDITE 5209

This is an epoxy-based system with a cure temperature range of 250 – 275°F (121 – 135°C). Again, it was found to contain DICY, so THF/DMF was used to prepare films for

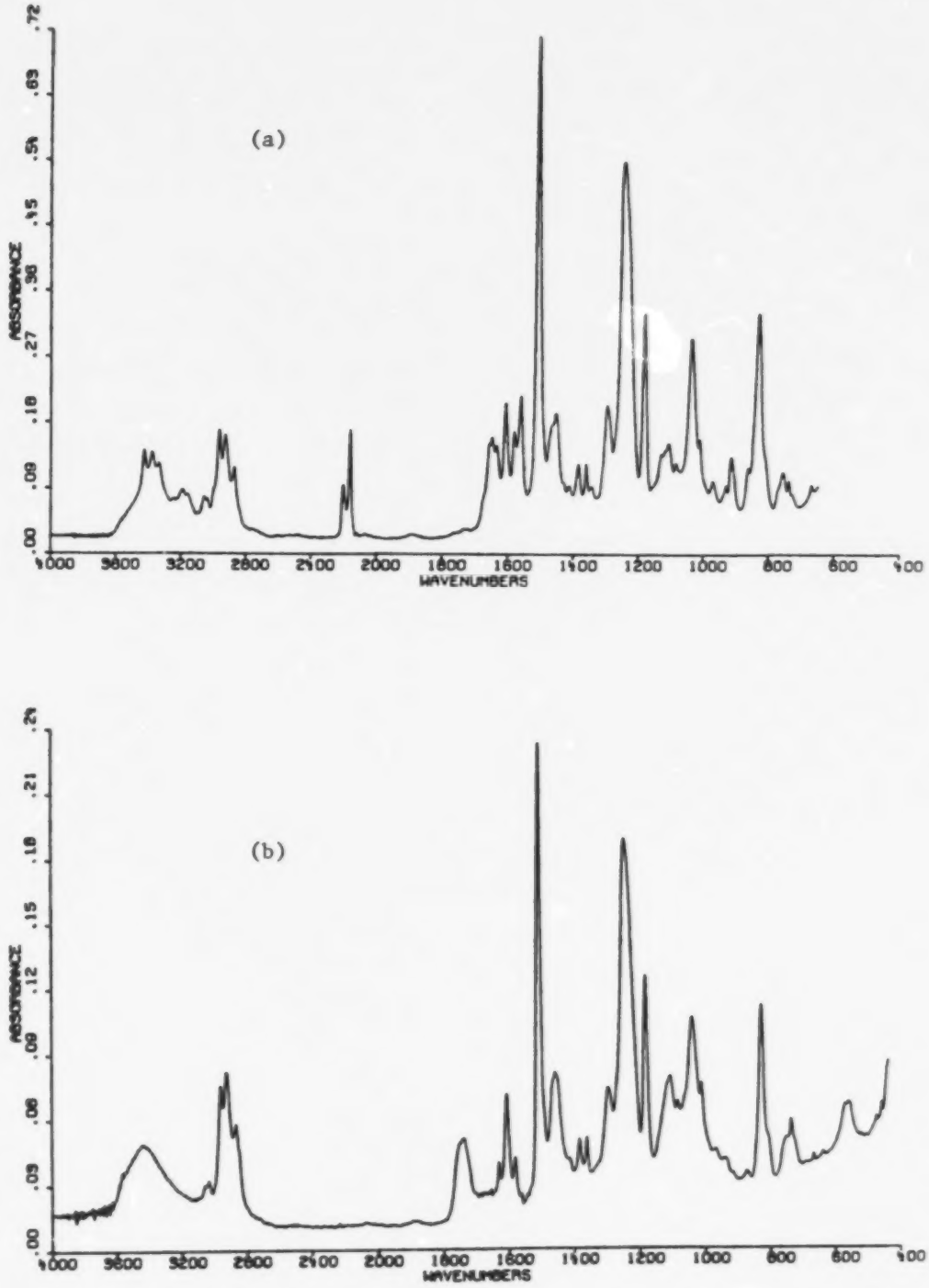


Figure 36. FT-IR transmission spectra of a thin film of Narmco 3203 resin: (a) uncured (b) cured.

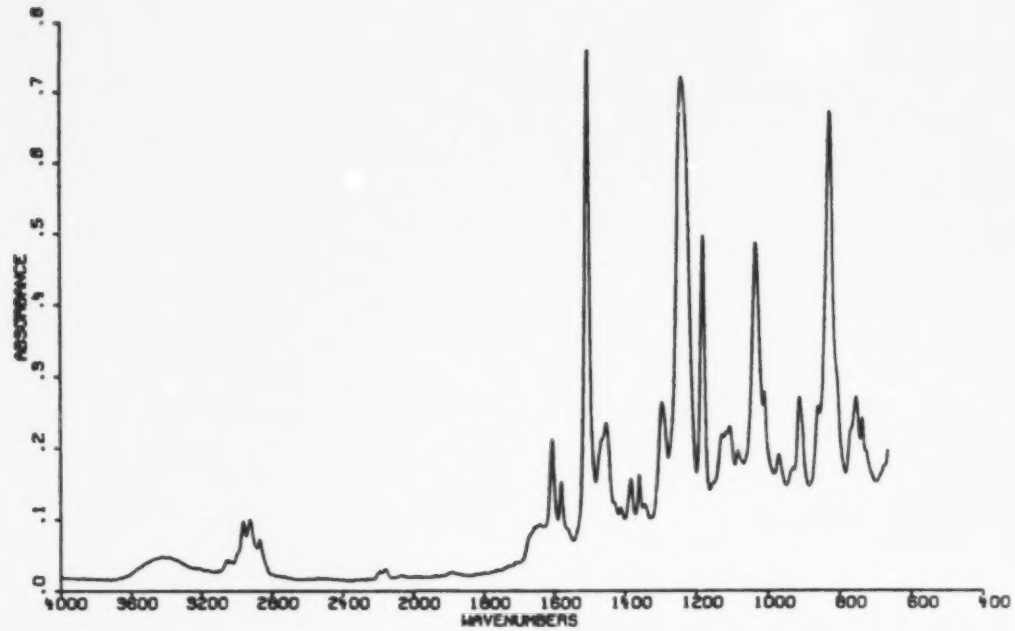


Figure 37. FT-IR attenuated total reflection spectrum of Narmco 3203/WC3000 prepreg.

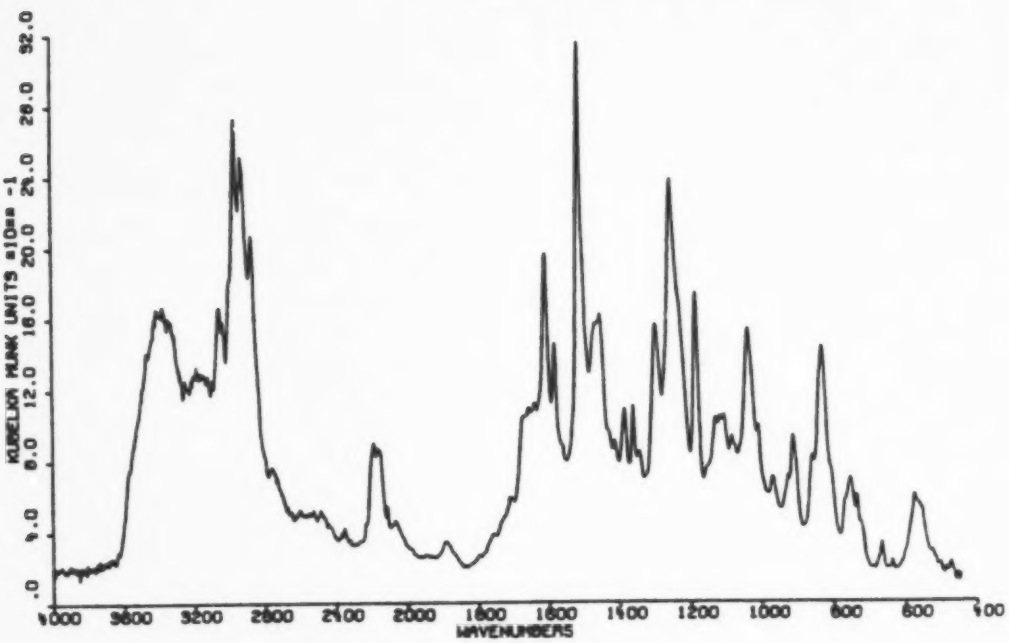


Figure 38. FT-IR diffuse reflection spectrum of Narmco 3203/WC3000 prepreg.

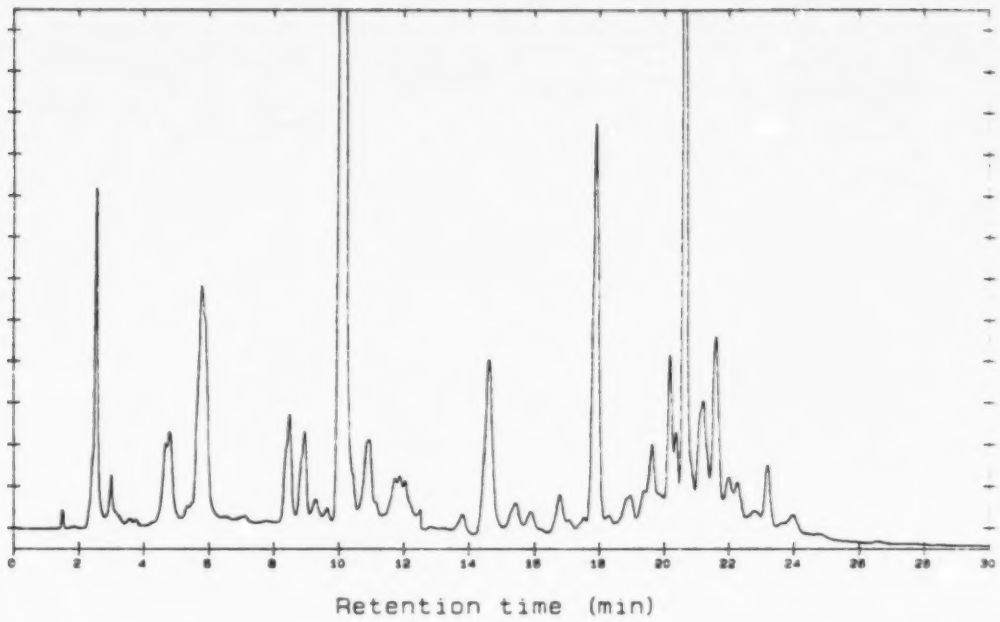


Figure 39. RPLC chromatogram of Narmco 3203 resin.

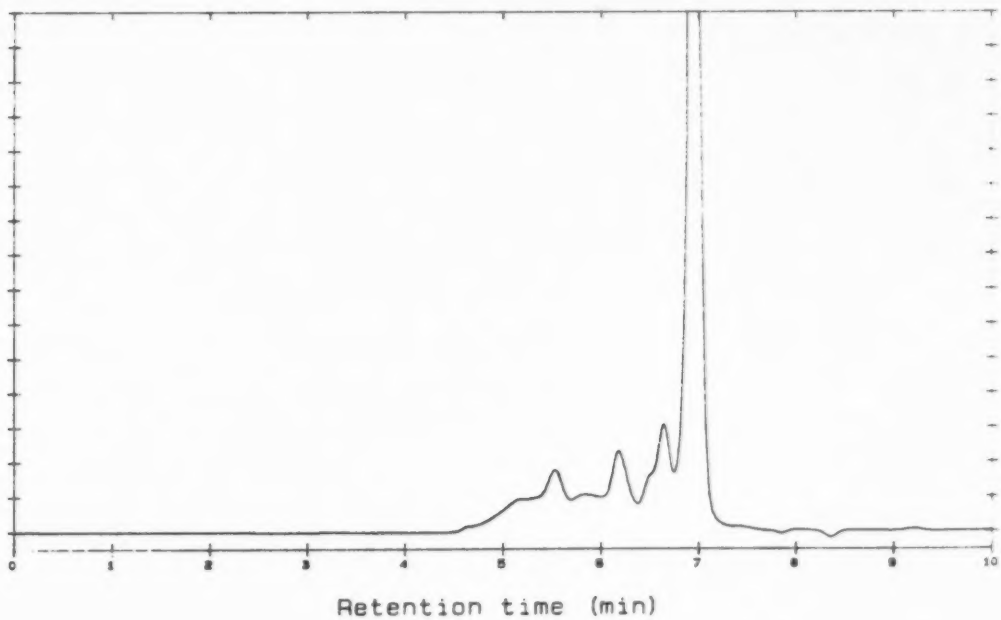


Figure 40. HPSEC chromatogram of Narmco 3203 resin.

IR spectroscopy. In this case, the extract was clear. The transmission spectra of uncured resin and resin cured for 3 hours at 130°C are shown in Figure 41. The major peaks correspond to a standard bisphenol A type epoxy, but the shape of the C-H bands do not correspond to this or any other common type. When the spectrum of Araldite 6010 was subtracted, the residual C-H peaks had the shape typical of an epoxy phenol Novolac (as in Ferropreg CE-9000-2). Thus this system appears to contain both a bisphenol A epoxy and a phenol Novolac type. In addition, there is a peak at 1730 cm^{-1} which does not disappear on curing, and this probably corresponds to a carbonyl-containing component.

As in the previous cases, the ATR spectrum (Figure 42) showed only very weak DICY peaks because of the non-homogeneous nature of the matrix. Again, a KRS-5 prism gave only slightly better results. Since the sample studied was reinforced with unidirectional carbon fibres, a good DR spectrum was obtained (Figure 43), but it is somewhat different from the transmission spectrum. Once again, this is no doubt a result of matrix heterogeneity.

The RPLC chromatogram is shown in Figure 44. Based on the previous examples and the IR results, the main peaks are tentatively assigned to DICY (2.5 min), epoxy phenol Novolac (8.4 and 8.9 min), and DGEBA from the bisphenol A epoxy (10.0 min). Other strong peaks are observed at 15.7 and 17.8 min.

The HPSEC chromatogram (Figure 45) shows a strong DICY peak at 6.9 min and at least seven weaker overlapping peaks between 4.5 and 6.5 min.

To summarize, this appears to be a rather complex system containing DICY, a bisphenol A epoxy, an epoxy phenol Novolac, and a carbonyl-containing component.

4.6 NARMCO RIGIDITE 5217

Like the three previous systems, this is an epoxy system cured at 250 – 300°F (121 – 150°C). It was found to also contain DICY, so THF/DMF was used for extraction; a clear solution was obtained. The reinforcement was unidirectional carbon fibres. IR spectra are given in Figures 46 to 48. The main components appear to be DICY and an epoxy phenol Novolac. Otherwise, the same comments apply as for Narmco Rigidite 5209.

The RPLC chromatogram (Figure 49) resembles that of Narmco 5209. It shows the DICY peak at 2.5 min and the peaks attributed to EPN at 8.4 and 8.9 min. However, the strong DGEBA peak at 10.0 min is absent, as are the peaks at 15.7 and 17.8 min. The HPSEC chromatogram (Figure 50) is also similar to that of Narmco 5209, but the peaks at 5.1 and 5.5 min are absent.

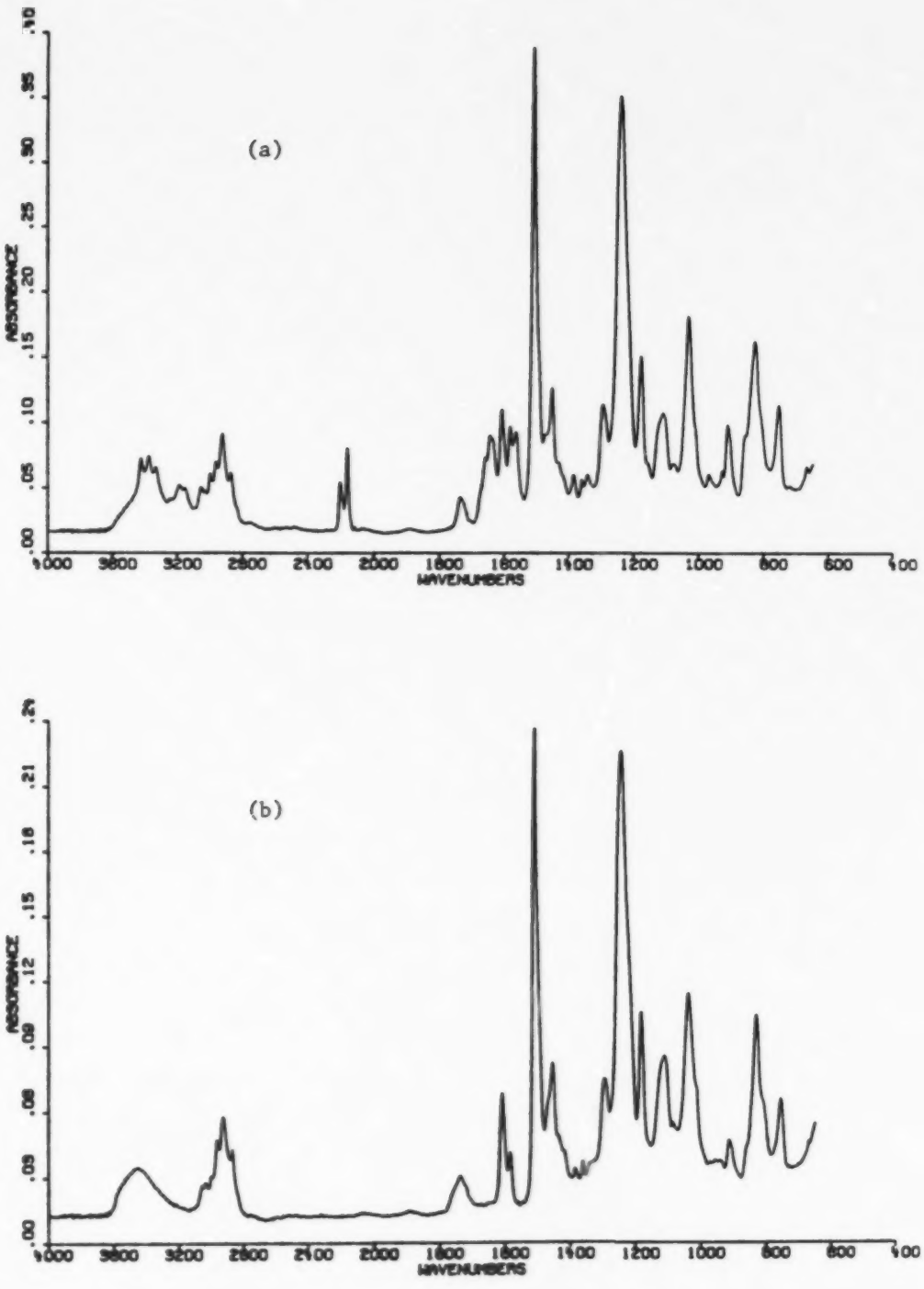


Figure 41. FT-IR transmission spectra of a thin film of Narmco 5209 resin: (a) uncured (b) cured.

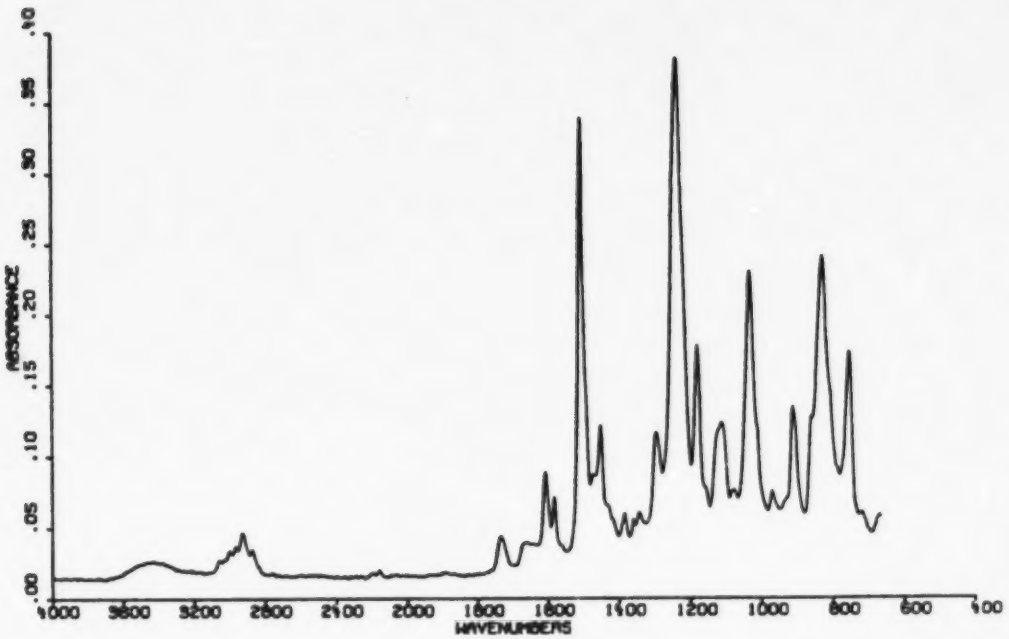


Figure 42. FT-IR attenuated total reflection spectrum of Narmco 5209 carbon-fibre prepreg.

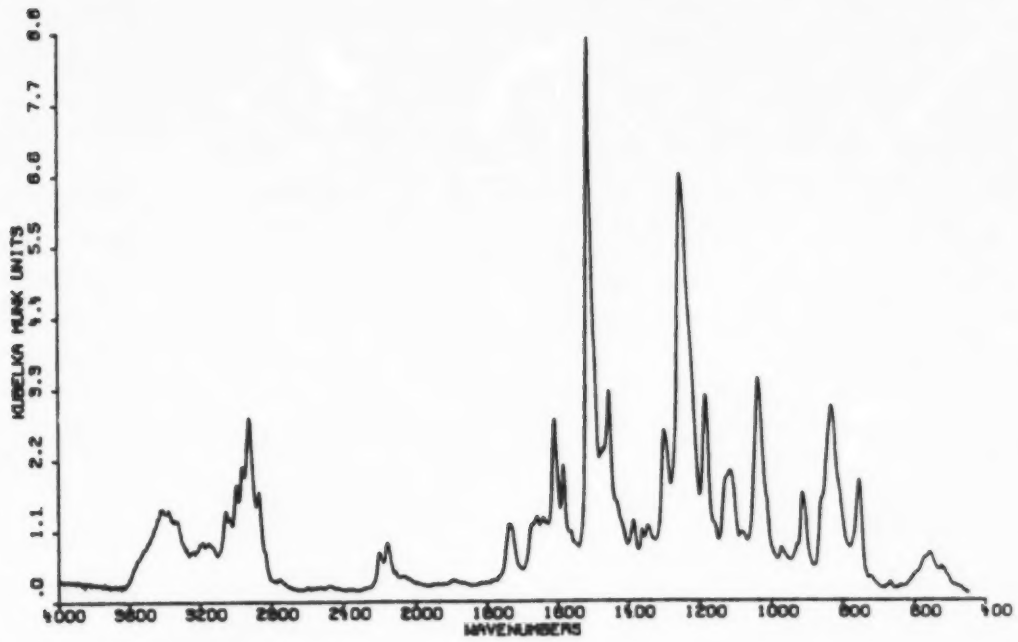


Figure 43. FT-IR diffuse reflection spectrum of Narmco 5209 carbon-fibre prepreg.

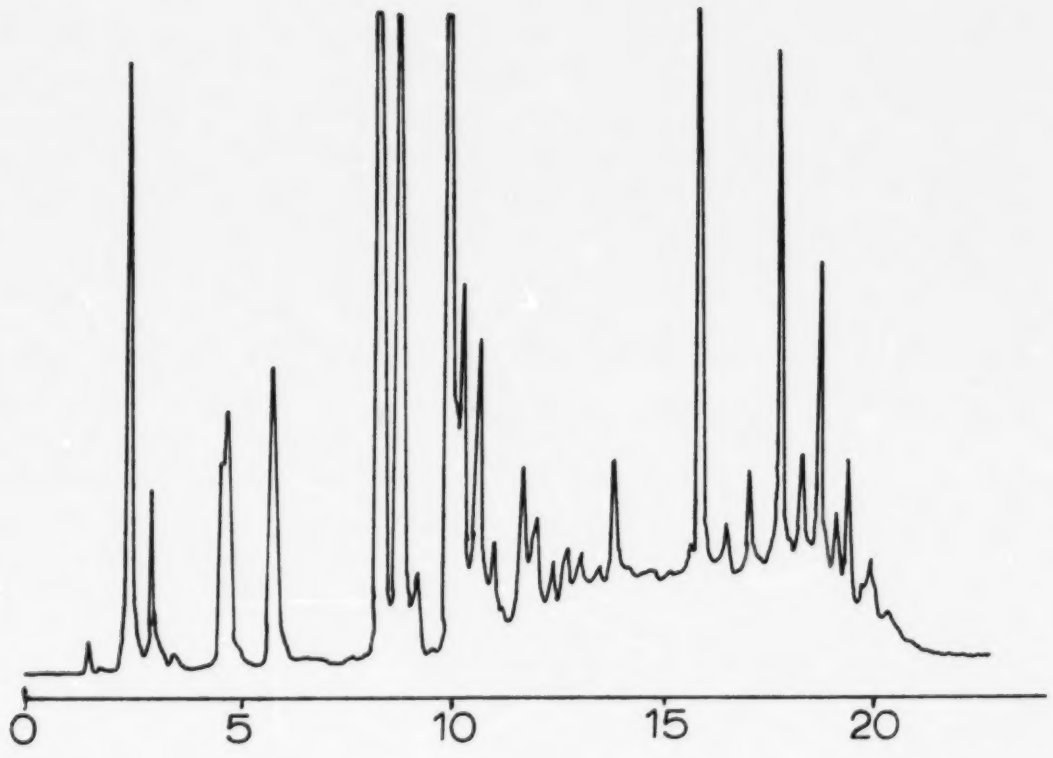


Figure 44. RPLC chromatogram of Narmco 5209 resin.

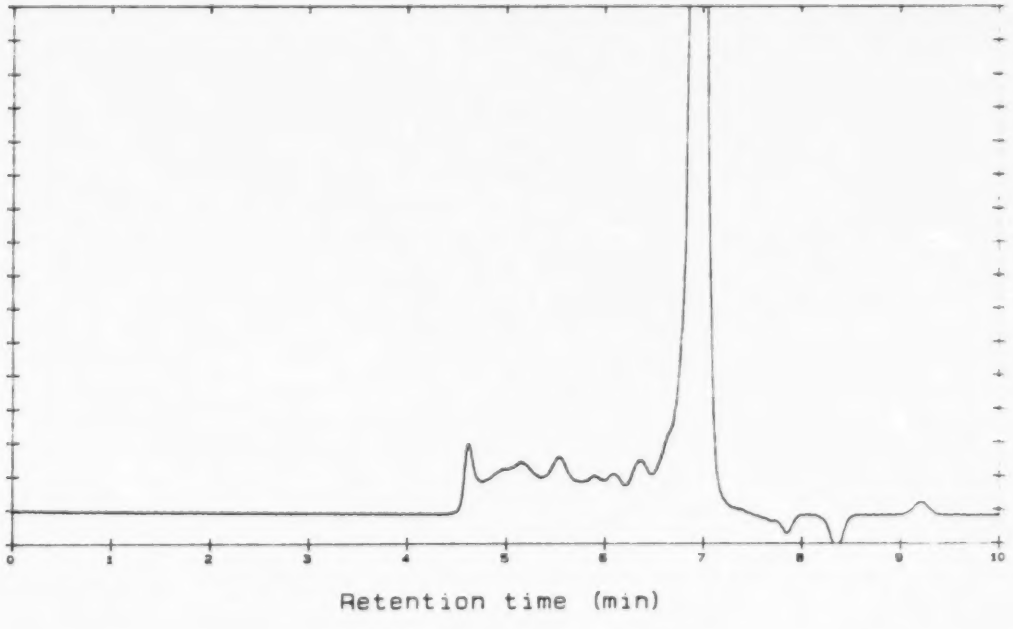


Figure 45. HPSEC chromatogram of Narmco 5209 resin.

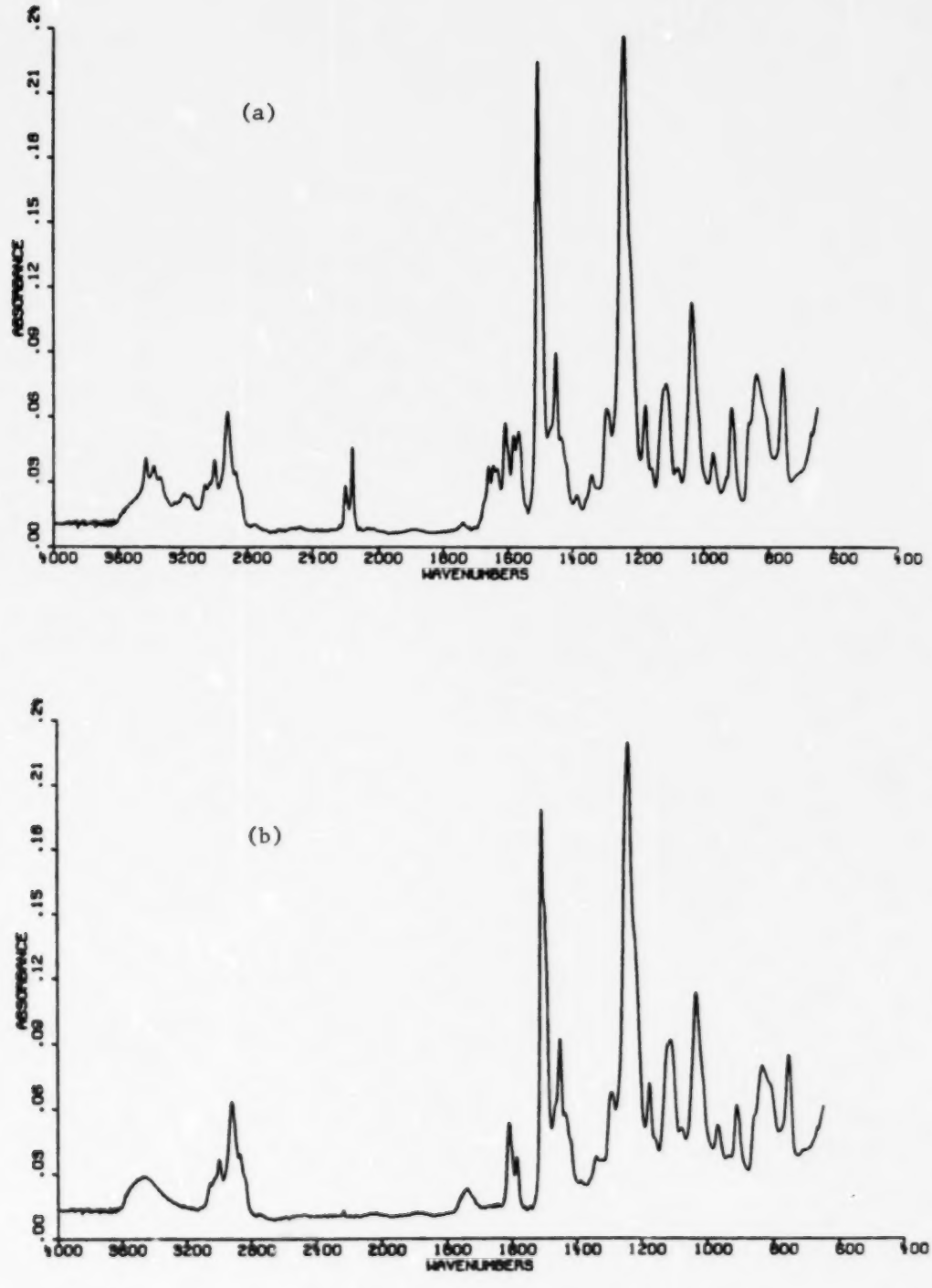


Figure 46. FT-IR transmission spectra of a thin film of Narmco 5217 resin: (a) uncured (b) cured.

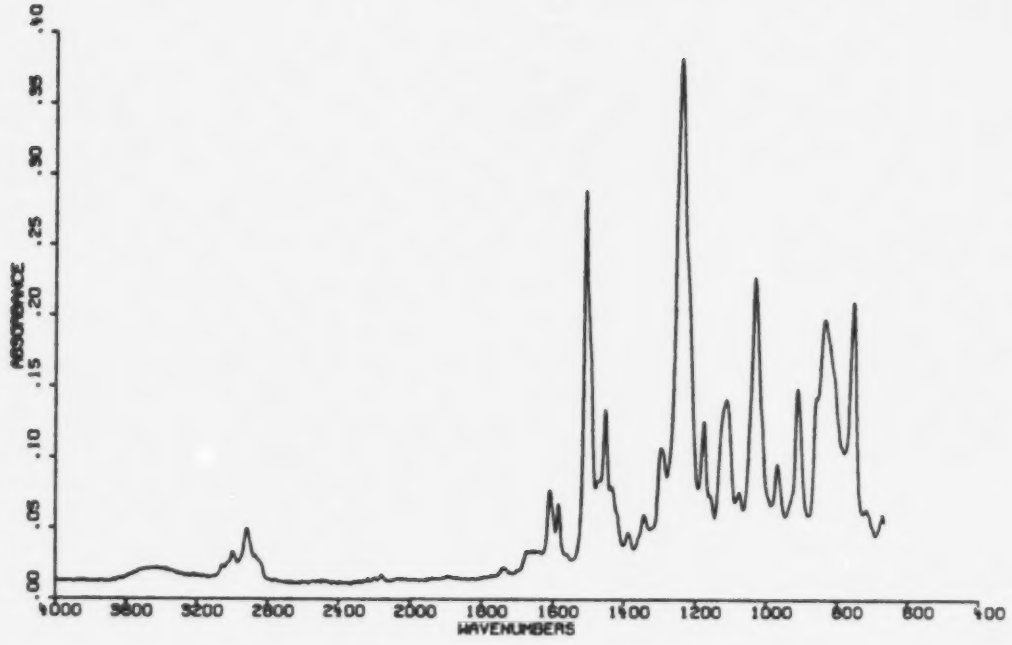


Figure 47. FT-IR attenuated total reflection spectrum of Narmco 5217 carbon-fibre prepreg.

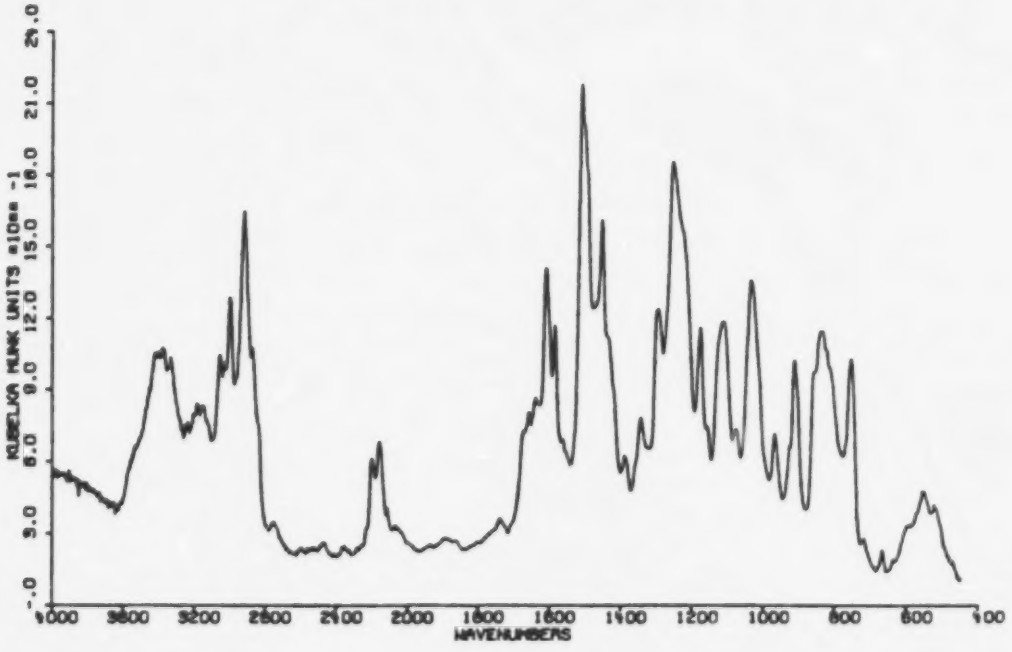


Figure 48. FT-IR diffuse reflection spectrum of Narmco 5217 carbon-fibre prepreg.

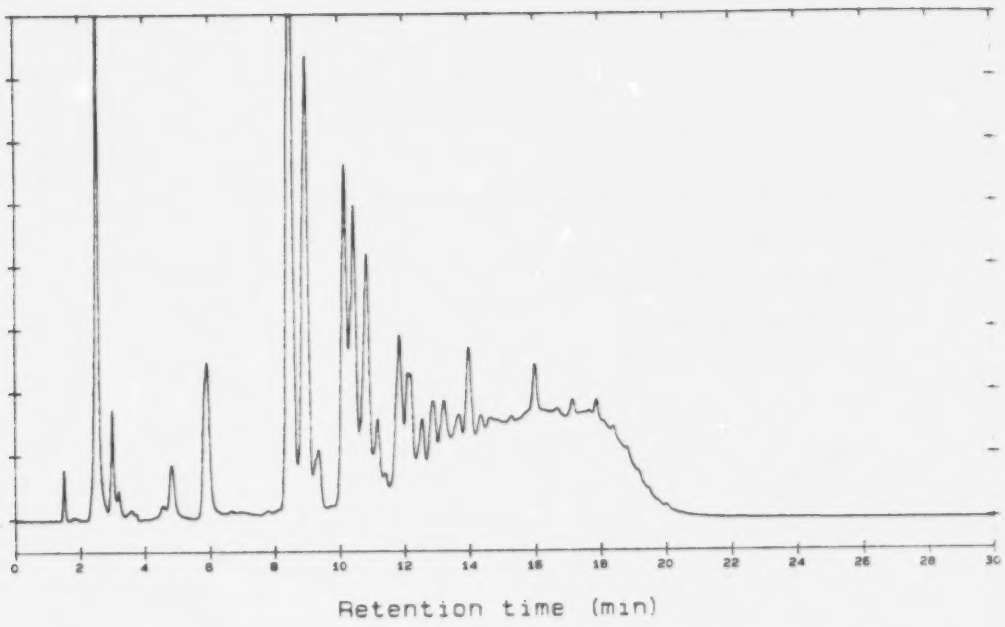


Figure 49. RPLC chromatogram of Narmco 5217 resin.

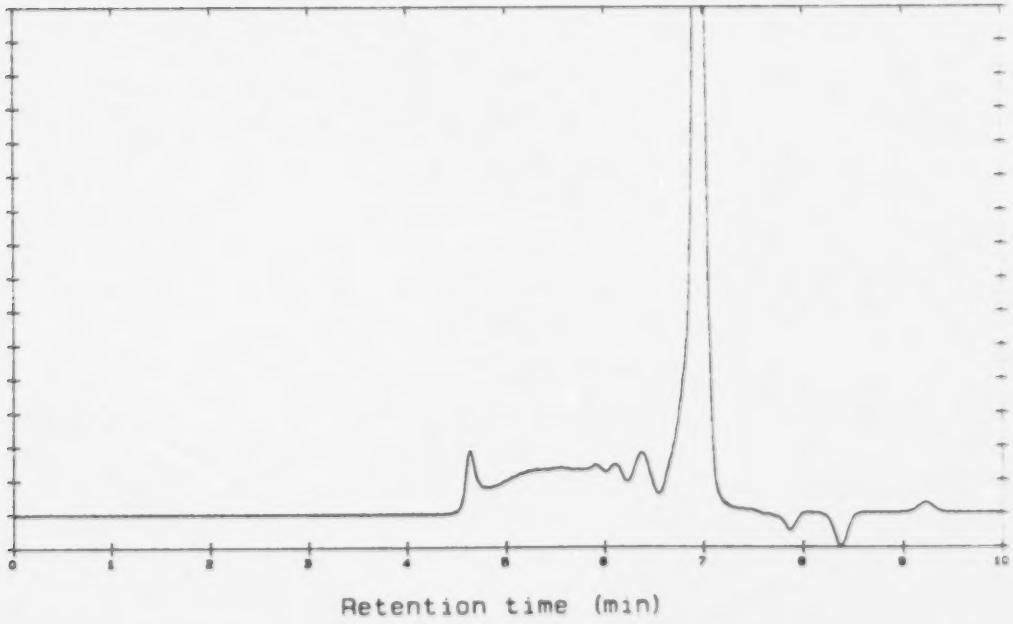


Figure 50. HPSEC chromatogram of Narmco 5217 resin.

It would appear that this system is a simpler version of Narmco 5209. It contains DICY and an epoxy phenol Novolac, but lacks the bisphenol A epoxy and the carbonyl-containing component.

4.7 NARMCO RIGIDITE 5245C

This product is different from all the previous ones in that it is based on a modified bismaleimide resin rather than epoxy. The reinforcement in the material investigated was unidirectional carbon fibres. Acetone was found to be a good solvent for extraction. As for most commercial products, the chemistry of Rigidite 5245C is not published, but it is thought to contain both epoxy and 'BT' resins [21]. The term 'BT' stands for 'bismaleimide-triazine', and these products, obtained by reacting bismaleimide with an isocyanate-containing monomer, have reactive isocyanate (-N=C=O) end groups.

Transmission IR spectra are given in Figure 51. As expected, they are quite different from those of the other systems, and a full analysis would require much more work. Of particular interest is the doublet at 2272 and 2238 cm^{-1}, which disappears completely on curing (3 hours at 180°C). This frequency corresponds very well to the isocyanate group [22]. Also interesting is the weak peak at 917 cm^{-1}, which also disappears on curing; it is almost certainly an epoxide ring peak. The shape of the C-H bands suggests a bisphenol A type resin. Thus, the IR spectra are in agreement with the composition proposed above. In theory, these peaks could be used for quantitative analysis of the isocyanate and epoxy groups, but it would be necessary to find a suitable reference peak (possibly the one at 1500 cm^{-1}). Both ATR (Figure 52) and DR (Figure 53) also gave good spectra.

The RPLC and HPSEC chromatograms are given in Figures 54 and 55 respectively. Both are quite detailed and would be useful for characterizing the system. However, because this system is so different from all the others studied, it is impossible to make conjectures concerning the identity of the peaks without further work. The peak at 1.5 min in the RPLC chromatogram indicates a highly polar constituent, and the shape of the HPSEC chromatogram shows that the components of this system are generally of higher molecular weight than those in the epoxy systems studied.

4.8 GENERAL DISCUSSION

The results given in this chapter show that the methods developed for Narmco 5208 can also be successfully applied to a variety of other systems to give useful information. However, the application is not always without problems, and caution must be exercised. Also, in most cases, some further work would be required before the methods could be

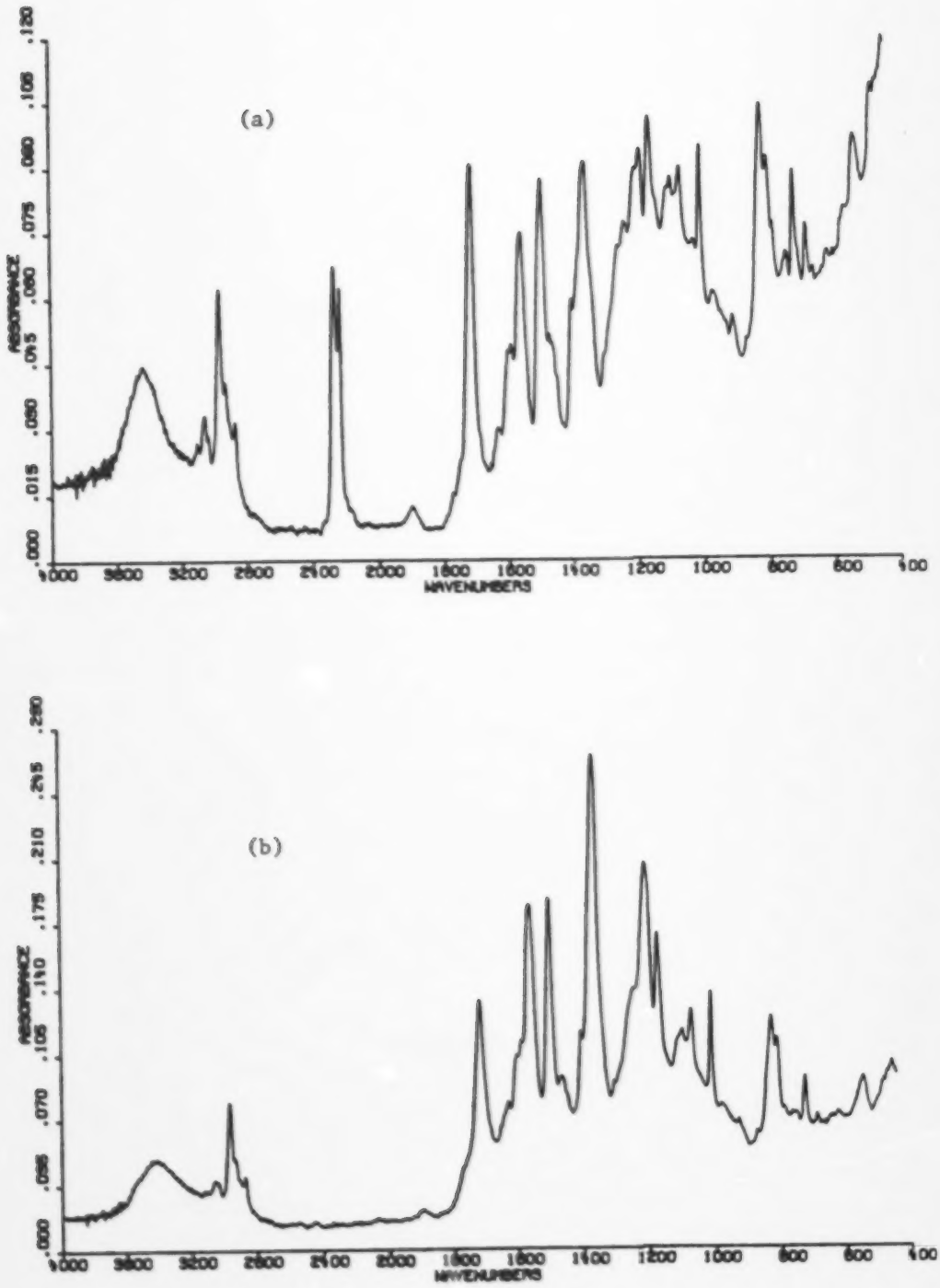


Figure 51. FT-IR transmission spectra of a thin film of Narmco 5245C resin: (a) uncured (b) cured.

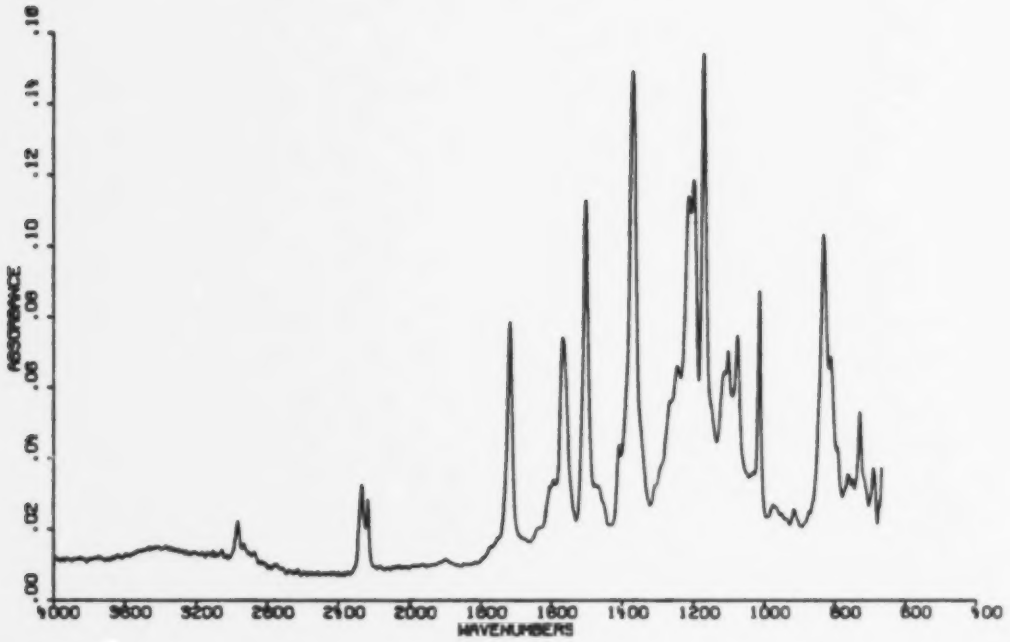


Figure 52. FT-IR attenuated total reflection spectrum of Narmco 5245C carbon-fibre prepreg.

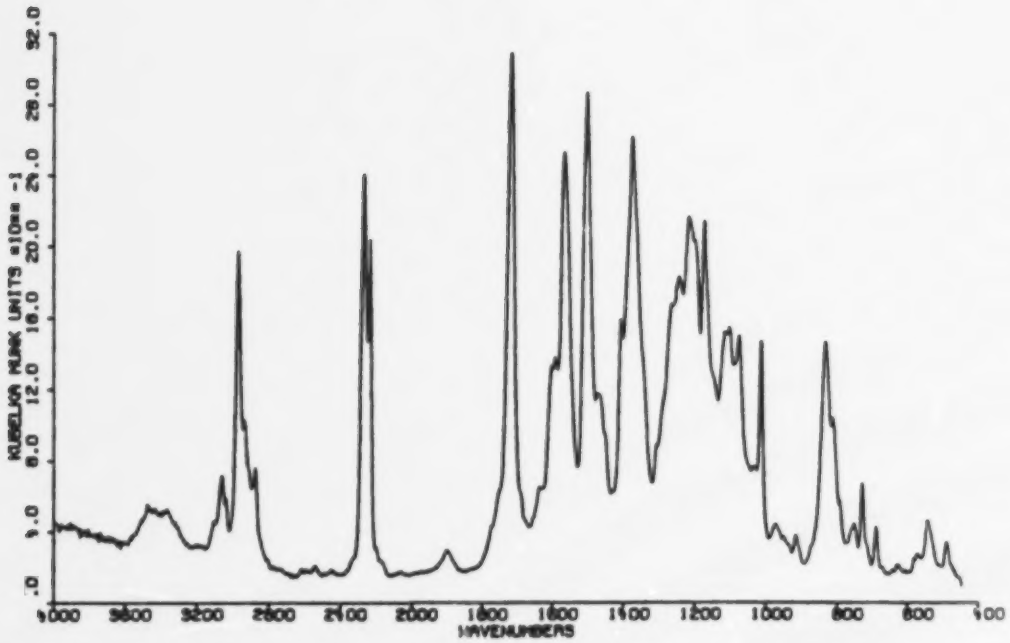


Figure 53. FT-IR diffuse reflection spectrum of Narmco 5245C carbon-fibre prepreg.

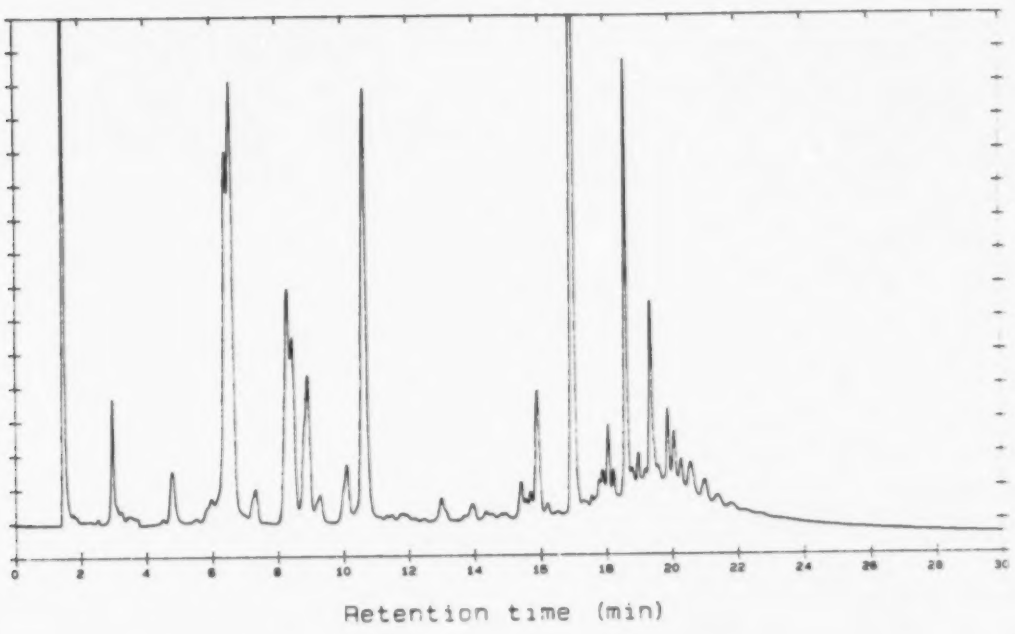


Figure 54. RPLC chromatogram of Narmco 5245C resin.

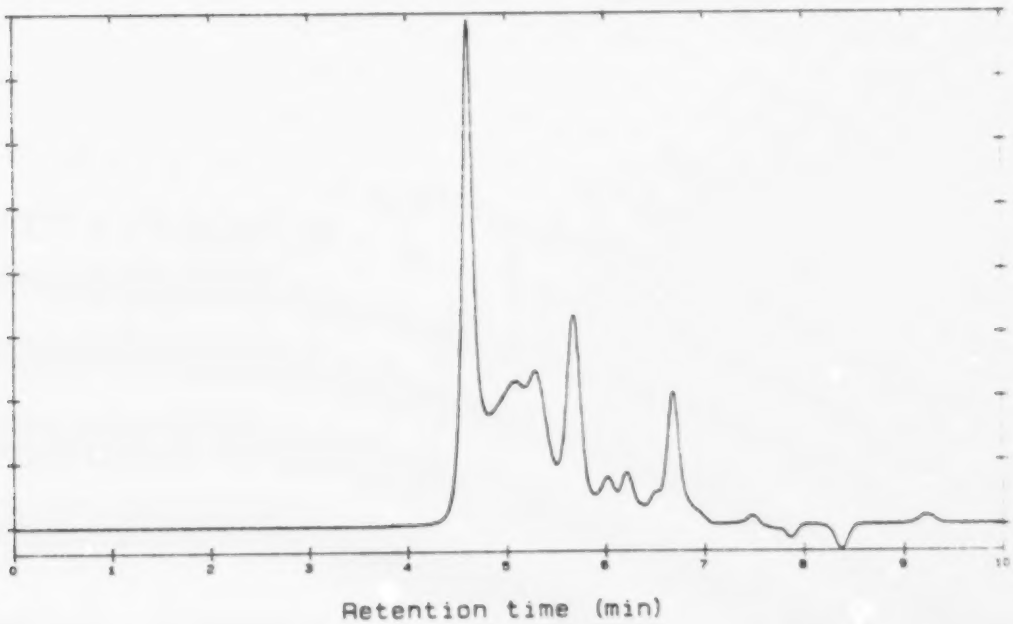


Figure 55. HPSEC chromatogram of Narmco 5245C resin.

used quantitatively. For example, in liquid chromatography the identity of the main peaks would have to be confirmed.

Systems containing DICY present particular problems because of limited solubility. For extraction of resin for transmission IR, a 50:50 mixture of THF and DMF seems to give better results than acetone, but care must be taken to ensure that the spectra are reproducible. Since the DICY tends to be insoluble in epoxy resins, the matrix in prepregs containing DICY is not homogeneous, and attenuated total reflection does not give reliable spectra because the surface layer is deficient in DICY. A further possible source of problems is the fact that DICY gives a peak at 929 cm^{-1} which overlaps with the epoxide ring peak at 915 cm^{-1} commonly used to monitor epoxy content.

In RPLC, systems containing DICY give a peak (possibly a reaction product) at 5.8 min, which would probably interfere with acetophenone if it were used as an internal standard. It might be necessary to find an alternative.

Generally speaking, prepregs based on epoxy resin reinforced with Kevlar or glass fibres (as opposed to carbon) do not give good IR spectra in diffuse reflection. This is because there is little reflection at the fibre-matrix interface, so the measured signal arises mainly from front-surface (Fresnel) reflection at the air-matrix interface.

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6. APPENDIX

RECOMMENDED METHODS FOR NARMCO 5208

RECOMMENDED PROCEDURE FOR QUANTITATIVE ANALYSIS OF NARMCO 5208 PREPREG BY TRANSMISSION FOURIER TRANSFORM INFRARED SPECTROSCOPY

(1) With clean scissors, and wearing gloves, cut a representative square of prepreg about 5 cm by 5 cm.

(2) With tweezers, carefully separate the prepreg from the plastic backing sheet and place it in a clean dry 250 mL Erlenmeyer flask.

(3) Add 25 mL of reagent grade acetone, stopper, and agitate gently for 15 minutes.

(4) Remove the graphite fibres with clean tweezers. The remaining solution contains about 25 mg/mL of resin.

(5) Prepare at least three (preferably five) clean windows of sodium chloride or potassium bromide. These should be of good quality with flat, highly polished surfaces. Repolish if necessary.

(6) In a location well protected from air currents, carefully deposit about 150 μL of resin solution in the centre of each window. A microsyringe can be used to control the amount. Stepwise addition is recommended to avoid having the solution flow over the edge. After each addition, let stand for a short time until the solvent evaporates. Do <u>not</u> blow with air and do not heat. Place the specimens under vacuum (without heating) for 15 to 30 minutes to remove residual solvent.

(7) Measure the infrared transmission spectrum for each specimen and convert to absorbance units. The strongest peak (1517 cm^{-1}) should have a maximum absorbance between 0.2 and 1.0, and there should be no obvious water vapour peaks in this region. If there are, they should be eliminated either by subtracting a reference spectrum of water vapour or by repeating the spectrum.

(8) Visually compare the spectrum with that of a typical batch (see, for example, Figure A-1) and check for any unusual features.

(9) Calculate the areas of the peaks of interest (Figure A-2) using the available software with baselines drawn between the appropriate valleys. The following limits are suggested but may be modified if necessary:

Aromatic ring peak (reference)	1545 - 1485 cm^{-1}
Sulphone peaks	1166 - 1046 cm^{-1}
Epoxide peaks	992 - 875 cm^{-1}

(10) Calculate sulphone and epoxide "indices" by dividing the peak areas by the area of the aromatic ring reference peak.

(11) The indices obtained for different specimens of the same prepreg sample should normally agree within about 2%. Specimens whose thickness is not uniform will give artificially high values. Specimens which give an index more than 5% higher than the lowest value should be rejected and repeated if necessary in order to give at least three good results for averaging.

(12) Compare the average values to the specifications to determine whether the batch is acceptable.

(13) Clean windows, syringes, etc. with acetone or a 50:50 mixture of acetone and toluene as soon as possible after use.

Note:

This method is suitable for typical B-stage resin. For more advanced prepreg, where the resin is less soluble, it is recommended to do a three-stage extraction using 50, 30, and 20 mL of acetone, followed by concentration of the combined extracts to a volume of about 25 mL on a rotary evaporator. A cloudy solution indicates a high degree of advancement and the results may be unreliable.

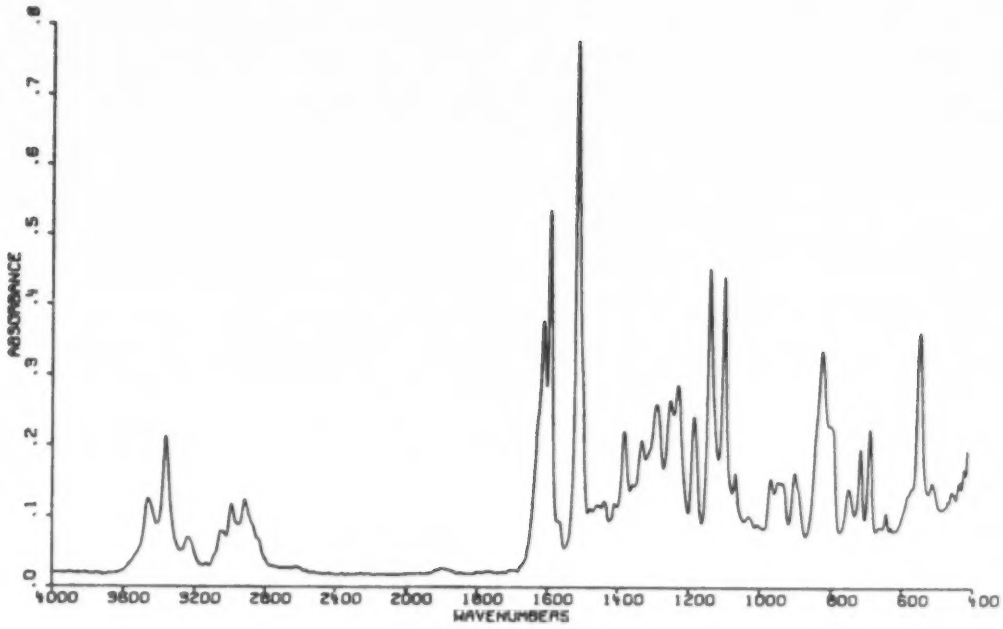

Figure A-1. Typical transmission FT-IR spectrum of Narmco 5208 resin.

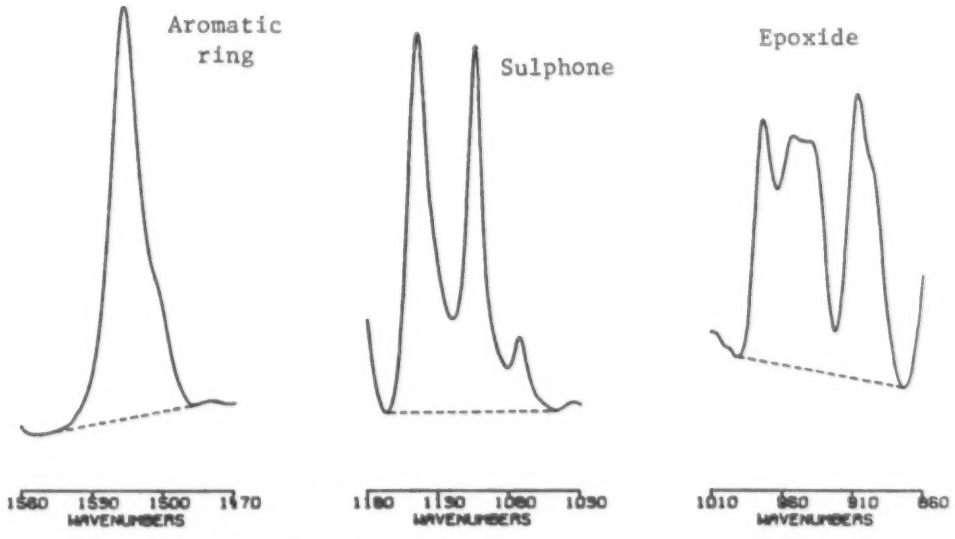

Figure A-2. FT-IR peaks used for quantitative analysis of Narmco 5208 resin.

RECOMMENDED PROCEDURE FOR QUANTITATIVE ANALYSIS OF NARMCO 5208 PREPREG BY ATTENUATED TOTAL REFLECTION FOURIER TRANSFORM INFRARED SPECTROSCOPY

(1) Make sure that the internal reflection accessory is installed in the spectrometer and properly aligned. A 45° germanium prism of length 50 mm is recommended.

(2) With clean scissors, and wearing gloves, cut two strips of prepreg of approximately the same size as the prism surface.

(3) Record the "background" spectrum using the clean prism only, accumulating as many scans as necessary to give an acceptable noise level.

(4) With tweezers, carefully remove the plastic backing sheet from the prepreg samples and place the freshly exposed surfaces in contact with the prism, one on each side. Install the pressure clamps and tighten. For normal prepreg, tightening with the fingers is sufficient. If the prepreg has lost its tack and flexibility, it may be necessary to use greater pressure.

(5) Record the spectrum with the prepreg in place and ratio against the background spectrum.

(6) Convert the spectrum to absorbance and check the intensity. The strongest peak (1517 cm^{-1}) should have a maximum absorbance between 0.2 and 1.0, and there should be no obvious water vapour peaks in this region. If there are, they should be eliminated either by subtracting a reference spectrum of water vapour or by repeating the spectrum.

(7) Visually compare the spectrum with a reference spectrum of a typical batch (Figure A-3) and check for any unusual features.

(8) Calculate the areas of the peaks of interest using the available software with baselines drawn between the appropriate valleys. The following limits are suggested but may be modified if necessary:

Aromatic ring peak (reference)	1545 - 1485 cm^{-1}
Sulphone peaks	1163 - 1043 cm^{-1}
Epoxide peaks	992 - 872 cm^{-1}.

(9) Calculate sulphone and epoxide "indices" by dividing the peak areas by the area of the aromatic ring reference peak.

(10) Measure at least three different specimens of a given prepreg sample. The spread between the lowest and highest values of a given index should not exceed 5%. If

so, more specimens should be measured in order to obtain at least three good results for averaging.

(11) Compare the average values to the specifications to determine whether the batch is acceptable.

(12) After each specimen, the prism should be cleaned with solvent (acetone or 50:50 acetone-toluene) and thoroughly dried. Cotton wool swabs are recommended for wiping the prism.

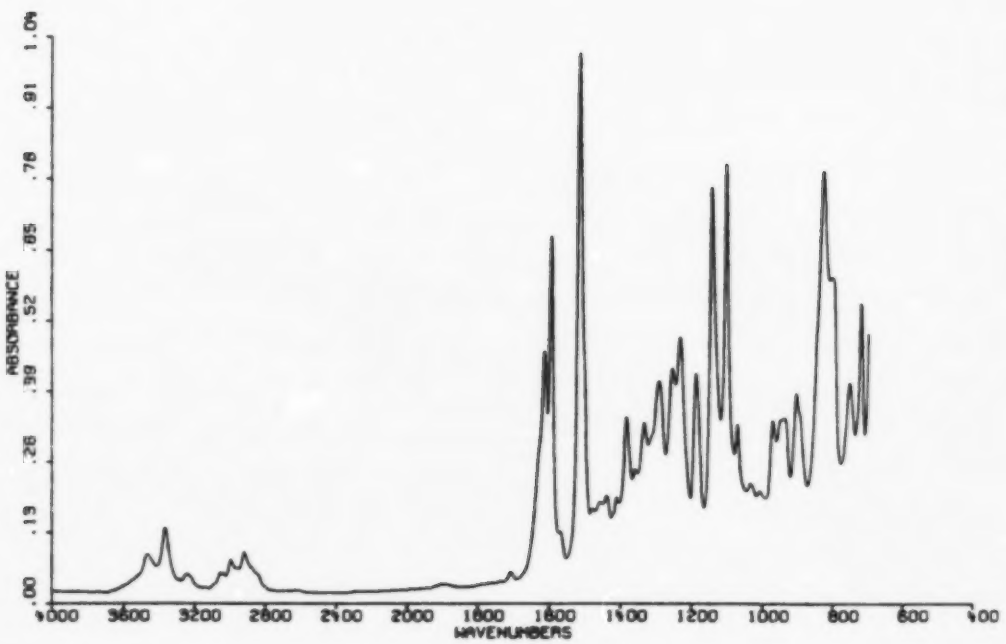

Figure A-3. Typical attenuated total reflection FT-IR spectrum of Narmco 5208 prepreg (45° germanium prism).

RECOMMENDED PROCEDURE FOR ANALYSIS OF CARBON-EPOXY COMPOSITES BY DIFFUSE REFLECTION FOURIER TRANSFORM INFRARED SPECTROSCOPY

(1) Make sure that the diffuse reflection accessory is installed in the spectrometer and properly aligned.

(2) Prepare a potassium bromide reference sample by filling the appropriate sampling cup with ground KBr and compacting with a clean spatula to give a smooth surface.

(3) Prepreg and cured laminate samples are measured using a horizontal support of adjustable height, so that the sample surface can be adjusted to the same height as the potassium bromide reference sample. Preliminary trials should be done to find the optimum height adjustment (maximum energy throughput).

(4) Cut samples about 1 cm x 1 cm using scissors (for prepreg) or a jigsaw (for cured laminate).

(5) Affix the sample to the support. Prepreg is usually tacky enough to adhere by itself when pressed in place. This can be done with the fingers if the plastic backing sheet is left in place; the plastic is then carefully removed to record the spectrum of the freshly exposed surface. For cured samples, double-sided adhesive tape can be used. Avoid touching the surface to be measured with the fingers.

(6) If the fibre reinforcement does not have a plain weave pattern, the quality of the spectrum may depend on the orientation of the sample. With a Harrick "praying mantis" accessory, best results are obtained if the principal fibre direction is parallel to the beam direction.

(7) Record spectra for both the KBr reference and the sample and take the ratio. Accumulate enough scans to obtain a good signal-to-noise ratio.

(8) If the spectrum is to be compared with transmission spectra, convert it to Kubelka-Munk units and do a baseline correction. This can then be compared to a transmission spectrum in absorbance units. See Figures A-4 and A-5 for typical spectra.

(9) Quantitative measurements are not recommended for diffuse reflection spectra of this type of sample.

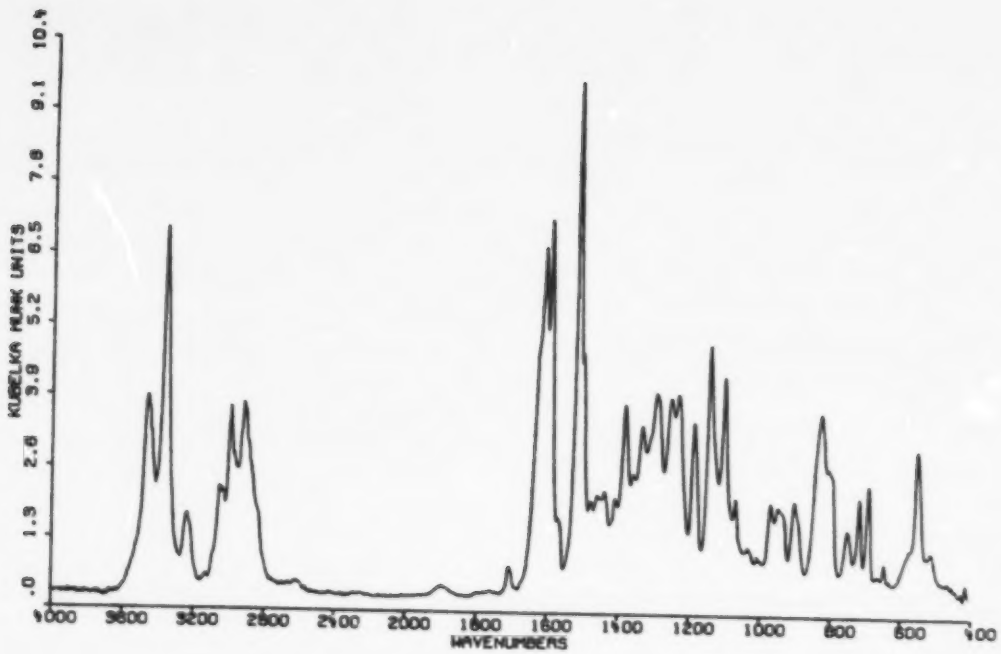

Figure A-4. Typical diffuse reflection FT-IR spectrum of Narmco 5208 carbon-fibre prepreg.

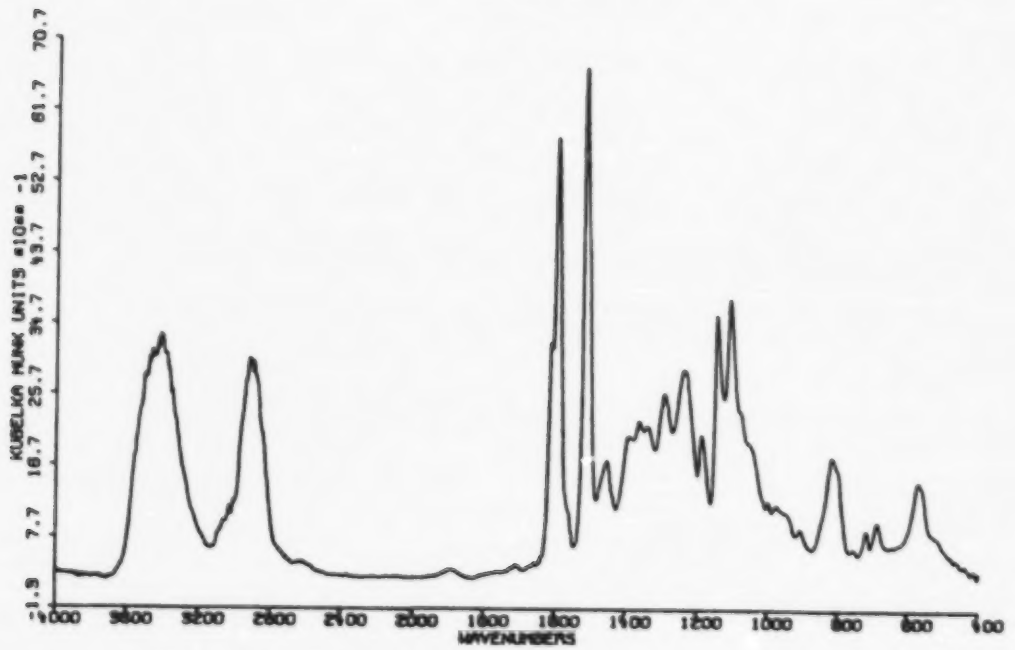

Figure A-5. Typical diffuse reflection FT-IR spectrum of cured panel made from Narmco 5208 carbon-fibre prepreg.

RECOMMENDED PROCEDURE FOR ANALYSIS OF NARMCO 5208 PREPREG BY LIQUID CHROMATOGRAPHY

I. Preparation of acetophenone standard solution:

(1) Weigh a stoppered 125 mL Erlenmeyer flask on an analytical balance.

(2) Add to the Erlenmeyer 0.5 mL of acetophenone.

(3) Weigh again to determine the weight of acetophenone.

(4) Add 50 mL of tetrahydrofuran.

(5) Weigh again to determine the weight of tetrahydrofuran.

(6) Calculate the concentration of acetophenone in THF (about 1.1% by weight).

(7) Keep the flask tightly stoppered when not in use to prevent evaporation of THF.

II. Preparation of sample for analysis:

(1) Weigh a 250 mL beaker on an analytical balance.

(2) With clean scissors, and wearing gloves, cut a representative square of prepreg about 5 cm by 5 cm.

(3) With tweezers, carefully separate the prepreg from the plastic backing sheet, place it in the beaker, and weigh again to determine the weight of the prepreg.

(4) Weigh a stoppered 125 mL Erlenmeyer flask.

(5) Add 1 mL of the standard solution of acetophenone to the Erlenmeyer.

(6) Weigh again to determine the weight of solution and hence the weight of acetophenone (about 0.01 g).

(7) Extract the prepreg in three stages with 50, 30, and 20 mL of THF. After each stage (15 minutes), transfer the THF solution to the Erlenmeyer, being careful to ensure that all is transferred.

(8) Put the beaker and fibres in an oven at 120°C for one hour and cool in a desiccator.

(9) Weigh the beaker to determine the weight of the graphite fibres without resin, and thus, by subtraction, the weight of the extracted resin (about 0.75 g).

III. Experimental conditions for reverse-phase liquid chromatography:

Column: C_{18} or C_8 bonded phase, for example, Varian MCH-5-n-CAP (30 cm long x 4.0 mm i.d.) or Hypersil MOS-1 (25 cm long x 4.6 mm i.d.). Both have 5 μm particles.

Injected volume: 5 μL (filtered).

Column temperature: 25°C.

Mobile phase flow rate: 1.0 mL/min.

Detector: UV at 230 nm.

Gradient: 50/50 ACN/H_2O to 100% ACN in 15 minutes (linear gradient), maintained for a further 15 minutes, then returned to the initial composition over a one-minute period. The column is equilibrated with the mobile phase for 25 minutes before injection.

The response of each peak (either area or height, preferably area) is measured and normalized according to the formula:

$$\text{Normalized response} = \frac{\text{Peak response}}{\text{Acetophenone peak response}} \times \frac{\text{Wt. acetophenone}}{\text{Wt. of resin}} \times 100$$

It is recommended to inject the solution three times and to take the average of the normalized response. Ideally, it is preferable to perform more than one extraction to have a more representative value.

A simpler method may be used based on the ratios of the areas (or heights) of the major peaks with respect to that of TGDDM. In this case, acetophenone is not needed, nor is accurate weighing of the sample, unless it is necessary to determine the resin content of the prepreg.

Approximate retention times (in minutes) for the important peaks in Narmco 5208 (Figures A-6 and A-7):

Peak	MCH-5-n-CAP	Hypersil MOS-1
DDS	4.3	3.4
Acetophenone (ACP)	7.7	5.1
Reaction product (RP)	10.7	7.2
TGDDM	12.7	8.5
DGEBA	14.1	10.1

IV. Experimental conditions for high-speed reverse-phase liquid chromatography:

These are similar to those described in the previous section except for:

Column: Varian Ultrafast C_{18}-3 (4 cm long x 4.6 mm i.d.), 3 μm particles.

Injected volume: 1 μL (filtered)

Flow rate: 2.0 mL/min

Gradient: 20/80 ACN/H_2O to 100% ACN in 3 minutes (linear gradient), maintained for a further 2 minutes, then returned to the initial composition within 0.1 minutes. The column is equilibrated with the mobile phase for 4 minutes before injection.

A typical chromatogram is given in Figure A-8. Approximate retention times are as follows:

Peak	Time (min)
DDS	1.1
Acetophenone (ACP)	2.3
Reaction product (RP)	3.4
TGDDM	3.6
DGEBA	3.8

V. Experimental conditions for high-performance size-exclusion chromatography:

Column: PLgel (Polymer Laboratories), 30 cm x 7.5 mm i.d., 5 μm particles

Eluent: THF

Flow rate: 1.0 mL/min.

Column temperature: 25°C.

Injected volume: 20 μL (filtered).

Detector: Refractive index or UV detector.

A typical chromatogram is given in Figure A-9. Peak areas are calculated based on vertical lines drawn from the valleys on either side of the peak to the overall baseline of the chromatogram. They are then divided by the total area of the chromatogram to obtain relative peak areas expressed as a percentage of the total area. Peaks 2 and 3 are not well resolved and may be combined for area calculation. In addition, a "degree of polymerization index" may be calculated as follows:

$$\text{DP Index} = \frac{\text{Combined area of peaks 1 to 4}}{\text{Combined area of peaks 5 and 6}}$$

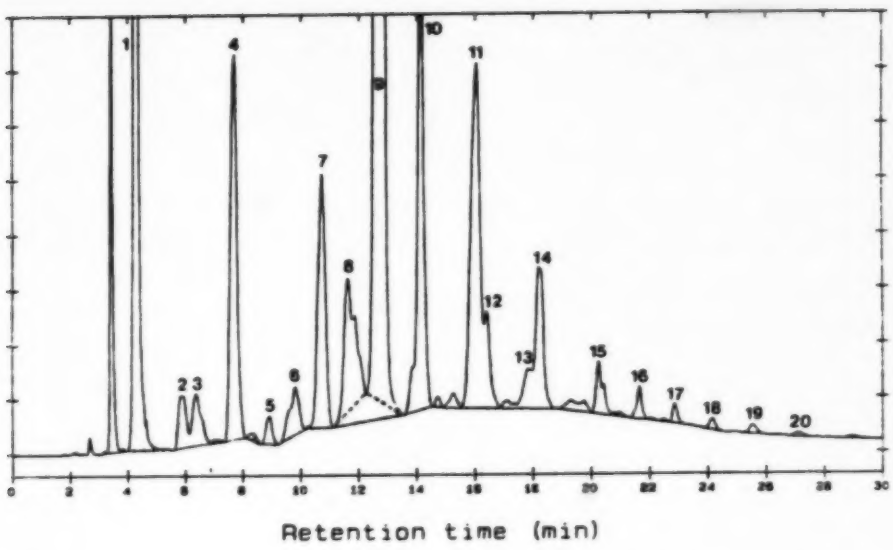

Figure A-6. Typical RPLC chromatogram of Narmco 5208 resin (MCH-5-n-CAP column).

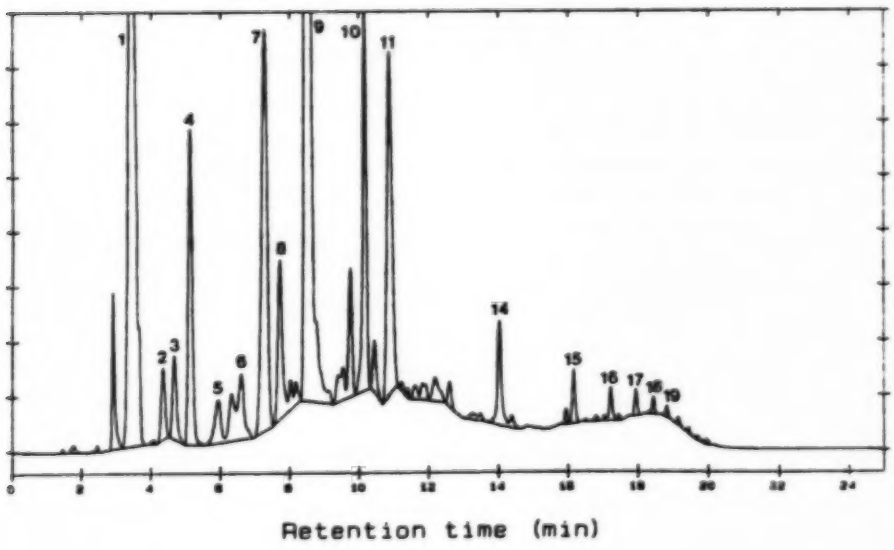

Figure A-7. Typical RPLC chromatogram of Narmco 5208 resin (Hypersil MOS-1 column).

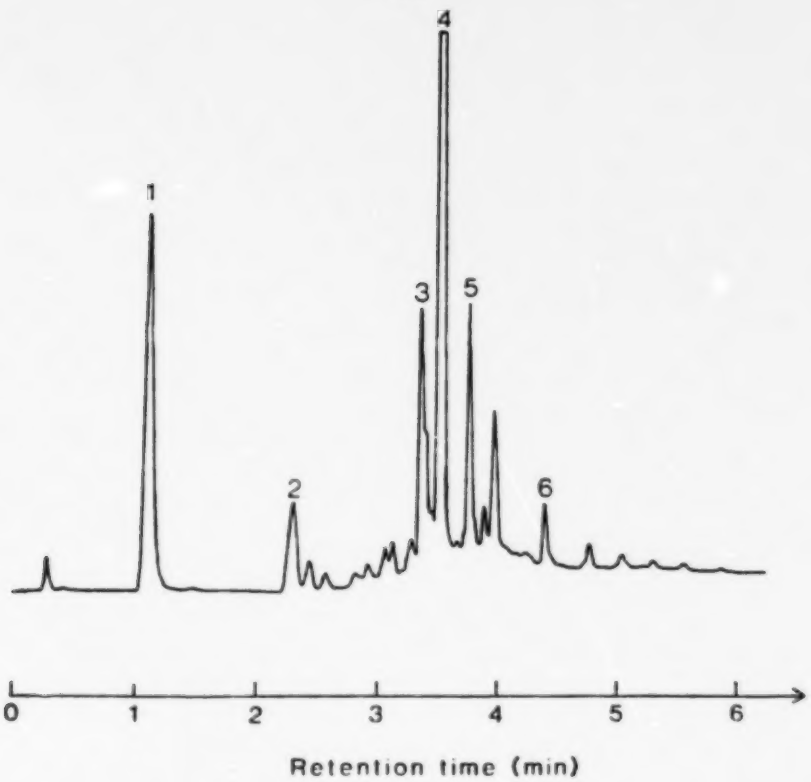

Figure A-8. Typical HS-RPLC chromatogram of Narmco 5208 resin (Varian Ultrafast C_{18}-3 column).

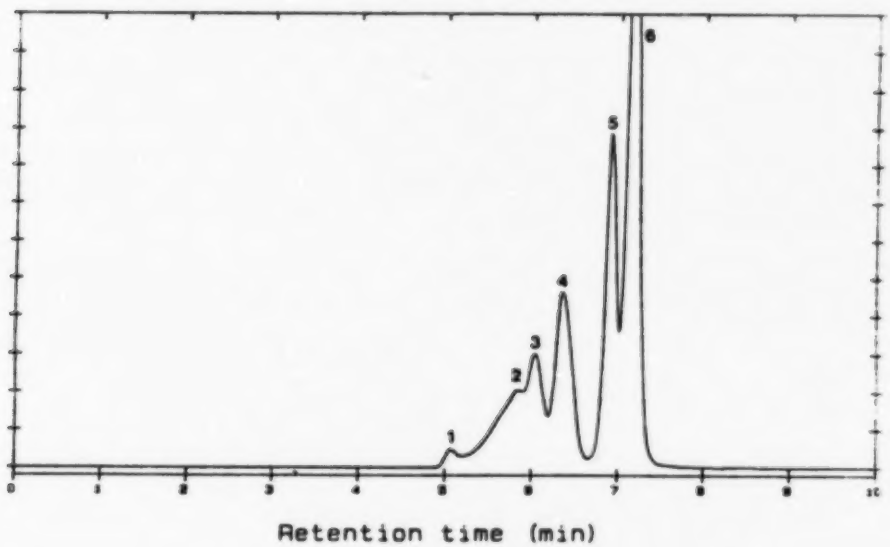

Figure A-9. Typical HPSEC chromatogram of Narmco 5208 resin (PLgel column).

RECOMMENDED PROCEDURE FOR ANALYSIS OF CARBON-EPOXY PREPREG BY THERMAL ANALYSIS (DSC AND TGA)

(1) With clean scissors, cut a small piece of the prepreg (3 mm x 20 mm).

(2) Put the sample in a platinum crucible and weigh. The mass of the sample must be between 30 and 40 mg.

(3) Record the thermogram at a heating rate of 5°C/min between 40°C and 320°C. Nitrogen is used as atmosphere and an empty platinum crucible is used as reference. If possible, a crucible filled with cured prepreg of weight similar to that the sample can be used. A typical curve is shown in Figure A-10.

(4) Calculate the enthalpy by measuring the area under the DSC curve between 130°C and 273°C.

(5) Weigh the crucible with the prepreg in order to determine the loss of resin during the DSC experiment.

(6) Transfer the same sample to the thermobalance and record a TG curve from room temperature to 800°C at a heating rate of 10°C/min using oxygen as atmosphere.

(7) The mass of resin is obtained at the inflection point on the TG curve at about 590°C as shown in Figure A-11.

(8) The mass found by TG is added to the mass lost during the DSC experiment and the sum is taken as the total resin mass and used to calculate the exact enthalpy of curing.

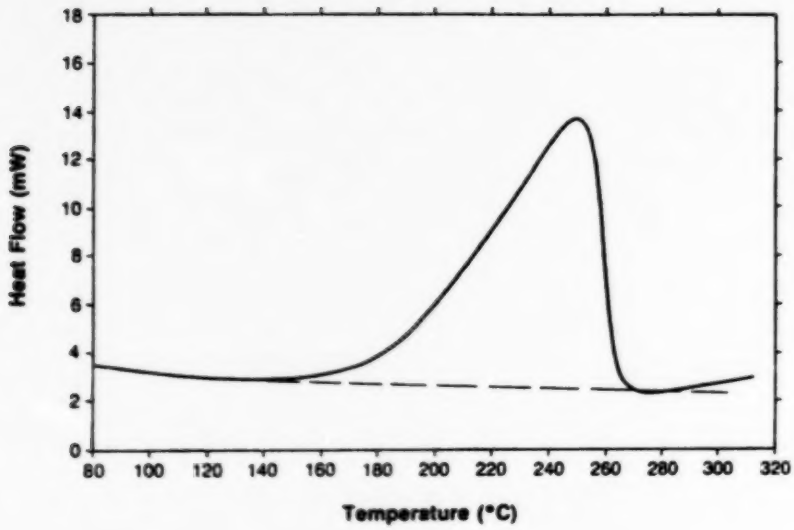

Figure A-10. Typical DSC curve of Narmco 5208 resin (5°C/min, nitrogen atmosphere).

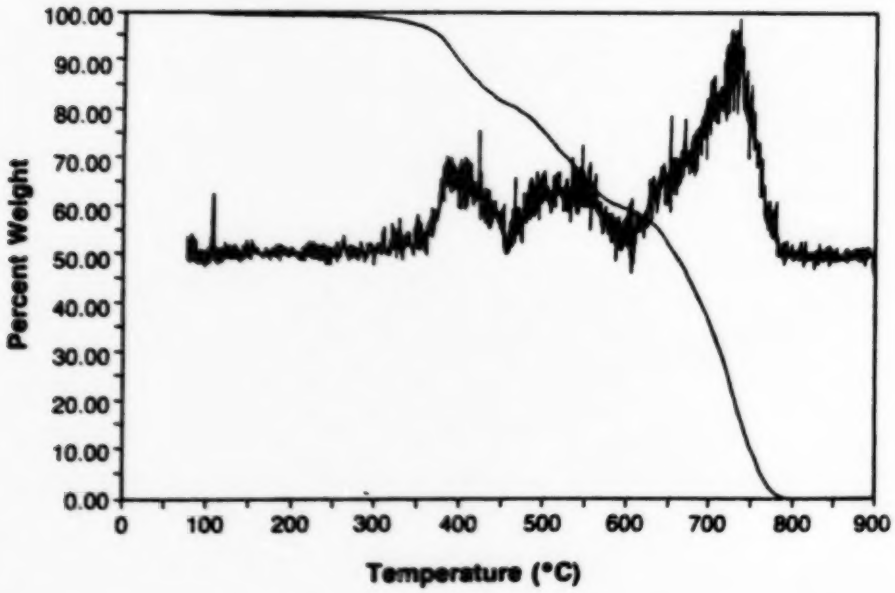

Figure A-11. Typical TGA curve of Narmco 5208 carbon-fibre prepreg (10°C/min, oxygen atmosphere).

RECOMMENDED PROCEDURE FOR ANALYSIS OF NARMCO 5208/WC3000 PREPREG BY PYROLYSIS - GAS CHROMATOGRAPHY

(1) With clean scissors, cut a small piece of the prepreg and weigh it using a micro-balance. The mass of the sample should be between 0.5 and 1.0 mg.

(2) Put the sample in the center of a 20 mm long quartz tube and place the tube in the probe.

(3) When the desired experimental conditions are obtained, put the probe in the pyrolyzer interface installed at the head of the chromatographic column.

(4) Suggested experimental conditions:

Temperature of the pyrolyzer interface: 200 °C.

Flow rate of helium in the interface: 150 mL/min.

Pyrolysis temperature: 650 °C.

Duration of the pyrolysis: 10 s.

Capillary column: DB-17, 30 m x 0.259 mm, film thickness 0.25 μm.

Column temperature program: 50°C to 60°C at 2°C/min, then 60°C to 250°C at 10°C/min.

Flow rate of helium in column: 1.5 mL/min.

Injector temperature: 250°C.

Detector: flame ionization detector (250°C).

(5) A typical chromatogram is shown in Figure A-12. For quantitative work, the areas of selected peaks are ratioed against the peak area of aniline (peak #2). Peaks 3, 4, and 7 are somewhat sensitive to the degree of cure of the prepreg. The ratio of aniline to phenol (peak #2 to peak #1) is a measure of the hardener/epoxy ratio.

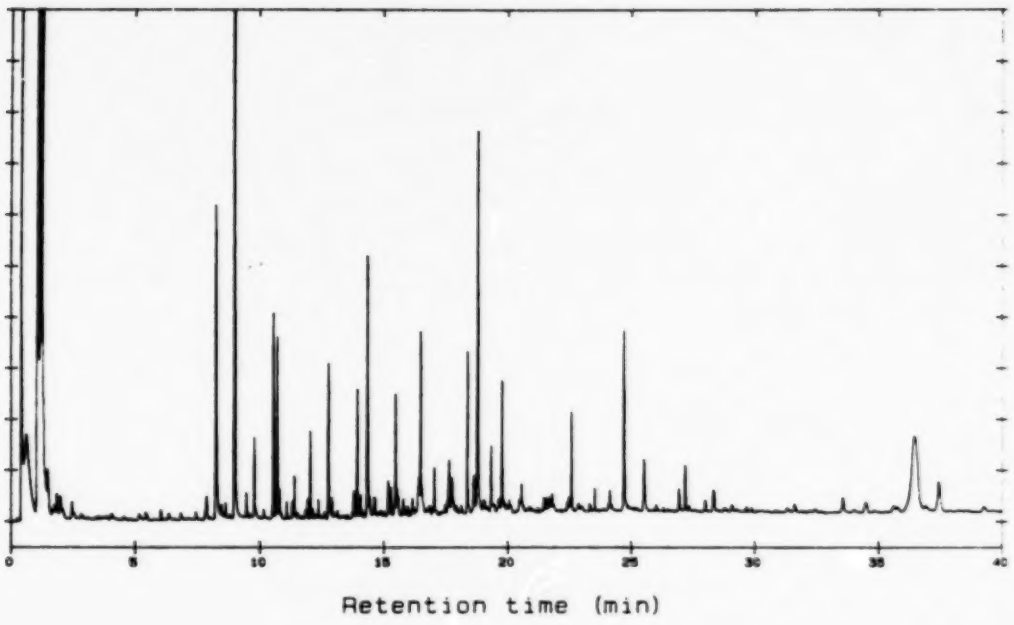

Figure A-12. Typical Py-GC chromatogram of Narmco 5208 carbon-fibre prepreg.